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DEVELOPMENT AND APPLICATION OF A METHOD FOR MEASURING REDUCED SULFUR COMPOUNDS IN PULP AND PAPER MILL WASTEWATERS

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by
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Acknowledgments

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PRESIDENT'S NOTE

In recent years, NCASI's technical program has addressed the identification of odorous compounds in wastewaters and their emission from wastewater treatment plants (WWTPs). To facilitate this, staff evaluated existing analytical methods and, where necessary, developed new methods aimed at identifying and quantifying wastewater constituents that may contribute to odors in and around treatment systems. As part of this effort, NCASI developed and applied NCASI Method RSC-02.02 for the determination of total (inorganic) sulfide, methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) in pulp and paper mill wastewaters. These reduced sulfur compounds have been associated with odors in WWTPs and are often tracked as part of odor reduction programs. This report presents the results of a single laboratory evaluation of the method to assess precision and accuracy, method blanks, linearity, and reproducibility. Concentrations of total sulfide, MeSH, DMS, DMDS, and DMTS measured in samples collected throughout the WWTPs of over twenty mills are also included. Information in this report will be of use to mill personnel who might wish to coordinate analyses of these compounds and to those tasked with reducing emissions or odors related to reduced sulfur compounds.

Ronald A. Yeske

June 2007

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MOT DU PRÉSIDENT

Depuis les dernières années, le programme technique de NCASI a examiné l'identification des composés odorants dans les eaux usées et leur émission par les systèmes de traitement des eaux usées (STEU). Pour ce faire, le personnel de NCASI a évalué les méthodes analytiques existantes et, lorsque cela s'avérait nécessaire, a développé de nouvelles méthodes visant à identifier et quantifier les composants des eaux usées susceptibles de contribuer aux odeurs à l'intérieur et autour des systèmes de traitement. Dans la même foulée, NCASI a développé et appliqué sa méthode RSC-02.02 pour déterminer les sulfures totaux (inorganiques), le méthyle mercaptan (MeSH), le sulfure de diméthyle (SDM), le disulfure de diméthyle (DSDM) et le trisulfure de diméthyle (TSDM) dans les eaux usées des fabriques de pâtes et papiers. Ces composés de soufre réduit sont associés aux odeurs dans les STEU et sont souvent surveillés dans le cadre des programmes de réduction des odeurs. Le présent rapport montre les résultats d'une évaluation en laboratoire de cette méthode afin d'en déterminer la précision et l'exactitude, les blancs de méthode, la linéarité et la reproductibilité. Le rapport contient également les concentrations de sulfures totaux, MeSH, SMD, DSDM et TSDM mesurées dans des échantillons collectés dans les STEU de plus de vingt fabriques. Le personnel des fabriques qui souhaite coordonner les analyses de ces composés et celui en charge de la réduction des émissions ou des odeurs reliées aux composés de soufre réduit trouveront utile l'information contenue dans ce rapport.

Ronald A. Yeske

Juin 2007

DEVELOPMENT AND APPLICATION OF A METHOD FOR MEASURING REDUCED SULFUR COMPOUNDS IN PULP AND PAPER MILL WASTEWATERS

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ABSTRACT

This research was initiated to develop and apply a method for determination of total (inorganic) sulfide, methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) in pulp and paper mill wastewater samples. NCASI Method RSC-02.02 utilizes separate preservations and injections for determination of total sulfide (zinc acetate at pH 10) and organic reduced sulfur compounds (ORSCs) (ascorbic acid at pH 2.5). All samples are acidified (pH <2.5) prior to direct injection on a gas chromatogram equipped with a pulsed flame photometric detector (PFPD). Daily calibration verifications yielded average recoveries of 106% for total sulfide (n=94) and average recoveries ranging from 95 to 102% for the ORSCs (n=42). Method blanks were free of the target analytes. Precision and accuracy were assessed using surrogate and matrix spike recovery experiments and replicate analyses. Surrogate recoveries for total sulfide, MeSH, DMS, DMDS, and DMTS in over 1077 samples ranged from 73 to 131%, with an average recovery of 106%. Matrix spike recoveries averaged 93, 106, 102, 112, and 96% for total sulfide, MeSH, DMS, DMDS, and DMTS, respectively. Precision results as reflected by pooled relative percent differences (RPDs) for duplicate analyses ranged from 2.1 to 5.3%. Storage stability studies indicated stability of the samples for up to 14 days. Injection pH significantly impacted recovery of total sulfide, with pH 2.5 yielding the highest recovery (96%). Studies to assess matrix and sampling variability yielded average relative standard deviations of 38.9% for total sulfide, 29.8% for MeSH, 20.6% for DMS, 34.2% for DMDS, and 41.0% for DMTS, well above the variability of ~5% observed for the analytical method.

Investigations conducted in conjunction with odor reduction studies at these mills yielded a wide range of results for reduced sulfur compound concentrations from similar locations within wastewater treatment plants (WWTPs). Median concentrations at primary clarifier outlets were 3.5 mg S/L for total sulfide, 38 μg S/L for MeSH, 66 μg S/L for DMS, 22 μg S/L for DMDS, and <20 μg S/L for DMTS. Median concentrations at the fronts of ASBs were 2.9 mg S/L for total sulfide, 60 μg S/L for MeSH, 68 μg S/L for DMS, 68 μg S/L for DMDS, and <20 μg S/L for DMTS. Median concentrations from midpoints of treatment were 0.29 mg S/L for total sulfide and <20 μg S/L for ORSCs. In final effluents, sample medians were <20 μg S/L for all target analytes.

KEYWORDS

analytical methods, dimethyl disulfide, dimethyl sulfide, effluent, methyl mercaptan, reduced sulfur compounds, total sulfide, wastewater

RELATED NCASI PUBLICATIONS

Special Report No. 05-01 (June 2005). *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters*.

NPRI Handbook 03.A.001 (March 2004). *Hydrogen sulphide – Pulp and paper*.

Methods Manual 02.B.011 (December 2002). *Method RSC-02.01: Reduced sulfur compounds by direct injection GC/PFPD*.

Technical Bulletin No. 849 (August 2002). *Compilation of speciated reduced sulfur compound and total reduced sulfur emissions data for kraft mill sources*.

DÉVELOPPEMENT ET APPLICATION D'UNE MÉTHODE POUR MESURER LES COMPOSÉS DE SOUFRE RÉDUIT DANS LES EAUX USÉES DES FABRIQUES DE PÂTES ET PAPIERS

BULLETIN TECHNIQUE N^{O} 933
JUIN 2007

RÉSUMÉ

Les auteurs du rapport ont initié cette recherche afin de développer et d'appliquer une méthode pour déterminer les sulfures totaux (inorganiques), le méthyle mercaptan (MeSH), le sulfure de diméthyle (SDM), le disulfure de diméthyle (DSDM) et le trisulfure de diméthyle (TSDM) dans les échantillons d'eau usée de fabriques de pâtes et papiers. Dans la méthode RSC-02.02 de NCASI, la préservation des échantillons et l'ajustement du pH préalable aux injections sont séparés pour déterminer les sulfures totaux (acétate de zinc à pH 10) et les composés organiques de soufre réduit (COSR) (acide ascorbique à pH 2,5). Tous les échantillons sont acidifiés (pH <2,5) préalablement à l'injection directe dans un chromatographe en phase gazeuse muni d'un détecteur photométrique à flamme pulsée (pulsed flame *photometric detector, PFPD)*. Les vérifications quotidiennes de calibration ont donné des pourcentages de récupération moyens de 106% pour les sulfures totaux (n=94) et des pourcentages de récupération moyens s'échelonnant de 95 à 102% pour les COSR (n=42). Les blancs de méthode ne contenaient pas les substances ciblées pour analyse. Les auteurs ont évalué la précision et l'exactitude en réalisant des expériences sur la récupération des étalons analogues (*surrogate*) et des matrices enrichies ainsi que des analyses des réplicas. Les pourcentages de récupération des étalons analogues pour les sulfures totaux, le MeSH, SDM, DSDM et TSDM dans plus de 1077 échantillons s'échelonnaient entre 73 et 131%, avec un pourcentage de récupération moyen de 106%. Les moyennes de récupération pour les matrices enrichies étaient de 93, 106, 102, 112 et 96% pour les sulfures totaux, le MeSH, le SDM, le DSDM et le TSDM, respectivement. La précision des résultats, représentée par le regroupement des différences relatives des pourcentages (relative percent differences, RPDs) pour les analyses des duplicatas, s'échelonnait de 2,1 à 5,3%. Les études de stabilité lors de l'entreposage indiquaient que la stabilité des échantillons se prolongeait jusqu'à 14 jours[1]. Le pH d'injection a produit un impact significatif sur la récupération des sulfures totaux. Le pH de 2,5 a produit la récupération la plus élevée (96%). Les études visant à évaluer la variabilité de la matrice et de l'échantillonnage a produit des écarts types relatifs moyens de 38,9% pour les sulfures totaux, 29,8% pour le MeSH, 20,6% pour le SDM, 34,2% pour le DSDM et 41,0% pour le TSDM. Ces valeurs se trouvent bien au dessus de la variabilité de ~5% observée pour la méthode analytique.

Les investigations réalisées en combinaison avec les études de réduction des odeurs dans ces fabriques ont produit un large intervalle de résultats pour les concentrations de composés de soufre réduit et ce, pour des endroits similaires dans les systèmes de traitement des eaux usées (STEU). Les concentrations médianes aux sorties de clarificateurs primaires étaient de 3,5 mg S/L pour les sulfures totaux, 38 μg S/L pour le MeSH, 66 μg S/L pour le SDM, 22 μg S/L pour le DSDM et <20 μg S/L pour le TSDM. Les concentrations médianes à l'avant des BSA (bassins de stabilisation aérés) étaient de 2,9 mg S/L pour les sulfures totaux, 60 μg S/L pour le MeSH, 68 μg S/L pour le SDM, 68 μg S/L pour le DSDM et <20 μg S/L pour le TSDM. Les concentrations médianes d'échantillons prélevés à mi chemin dans les systèmes de traitement étaient de 0,29 mg S/L pour les sulfures totaux et <20 μg S/L pour les COSR. Dans les effluents finaux, les médianes des échantillons étaient de <20 μg S/L pour toutes les substances ciblées pour analyse.

[1] Il s'agit du délai de conservation (N.d.T.)

MOTS CLÉS

Méthodes analytiques, disulfure de diméthyle, sulfure de diméthyle, effluent, méthyle mercaptan, composés de soufre réduit, sulfures totaux, eau usée

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

Rapport spécial n^{o} 05-01 (juin 2005). *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters*.

NPRI Handbook 03.A.001 (mars 2004). *Hydrogen sulphide – Pulp and paper*.

Methods Manual 02.B.011 (décembre 2002). *Method RSC-02.01: Reduced sulfur compounds by direct injection GC/PFPD*.

Bulletin technique n^{o} 849 (août 2002). *Compilation of speciated reduced sulfur compound and total reduced sulfur emissions data for kraft mill sources*.

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DEVELOPMENT AND APPLICATION OF A METHOD FOR MEASURING REDUCED SULFUR COMPOUNDS IN PULP AND PAPER MILL WASTEWATERS

1.0 INTRODUCTION

Odor is an ongoing issue for many pulp and paper facilities and an important part of many mill environmental management programs. Anti-nuisance laws and permit requirements that address fugitive odors are becoming more common and pulp and paper mills are often under pressure to control odors. Historically, most of the attention in the pulp and paper industry has been on kraft mills and the reduced sulfur compounds (RSCs) generated during kraft pulping and regulated as total reduced sulfur (TRS). TRS includes hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). As process emissions of RSCs have been reduced, emissions of RSCs from wastewater treatment plants (WWTPs) have become an issue at many mills. To better understand the factors that influence releases of RSCs to the air, a simple, accurate, and sensitive method to measure RSCs in wastewater samples was developed (Gholson, Hoy, and Chambers 2002). Development of additional methods to assess odorous compounds in air and water (Cook and Hoy 2003) and studies to develop effective models for predicting air emissions are ongoing. NCASI has developed, evaluated, and applied analytical methods for measuring RSCs, volatile fatty acids, and other odorous compounds at WWTPs. These research efforts indicate that RSCs, specifically total sulfide, MeSH, DMS, DMDS, and dimethyl trisulfide (DMTS), frequently cause odors associated with WWTP operations. Accurate, reproducible measurement of sulfide and other reduced sulfur species in pulp and paper mill wastewaters is of considerable importance to the industry.

NCASI developed Method RSC-02.01, a gas chromatography (GC) pulsed flame photometric detector (PFPD) method for the analysis of RSCs in aqueous samples at concentrations of 20 to 1000 μg S/L (Gholson, Hoy, and Chambers 2002). Since its development, the method has been revised and used to measure RSCs in a variety of aqueous phase samples from many WWTPs. This report discusses the development and application of NCASI RSC-02.02, including quality assurance and control data, WWTP sample analysis, sample preservation studies, and efforts to adapt the method for determination of freely available sulfide.

1.1 Analytical Methods for Reduced Sulfur Compounds in Aqueous Samples

The chemical nature of RSCs makes them a challenge to measure. The main difficulties encountered during determination of RSCs have been reviewed (Wardencki 1998) and can be summarized as the need to detect highly reactive compounds at low concentrations. Determination of RSCs is challenging due to their absorptive, adsorptive, photo reactive, volatile, biologically active, and oxidative properties that can lead to losses during sample collection, storage, and analysis. For example, aerobic biological activity can remove sulfide, while anaerobic activity can generate sulfide. The polar nature of these compounds (especially sulfide and MeSH) makes them attractive to active sites common to surfaces (e.g., metal) encountered during sampling and analysis.

Sulfide determinations are, by necessity, method defined because sulfide assumes various forms depending on sample pH, temperature, ionic strength, and the biological constituents present. Table 1.1 presents a glossary of terms that define various forms. Total sulfide is defined here as dissolved hydrogen sulfide plus hydrosulfide ion plus acid soluble metallic sulfide and sulfide weakly associated with organics in the sample. S^{2-} is considered to be present in negligible amounts unless sample pH is above 14. To obtain a measurement of dissolved sulfide, samples undergo either flocculation or filtration prior to analysis. Dissolved sulfide includes H_2S (un-ionized sulfide) and HS^- (ionized sulfide). Some methods, for example Hach Method 1851 (Hach Company 2003), recommend

sample centrifugation and analysis of the supernatant for determination of dissolved sulfide. Un-ionized H_2S has been calculated using the dissolved sulfide concentration, sample pH, and practical ionization constant for H_2S. Freely available sulfide varies from dissolved sulfide in that it also includes sulfides which may dissociate from organics readily in the matrix and therefore be freely available as sulfide. The acid soluble metallic sulfides are any of the metal sulfides that are soluble in acid. For example, iron sulfide (FeS) is commonly present in wastewaters. The organic reduced sulfides include any of the various organic compounds that contain sulfide, and the organic reduced sulfur compounds (ORSCs) commonly detected in wastewaters include MeSH, DMS, DMDS, and DMTS. Sulfides in all the forms listed in Table 1.1 may be anticipated in pulp and paper mill wastewaters.

Table 1.1 Glossary of Terms for Sulfide Compounds

Parameter	Description
Total sulfide	Dissolved H_2S and HS^-, acid-soluble metallic sulfides, and sulfide weakly associated with organics
Dissolved sulfide	Sulfide remaining after suspended solids have been removed by flocculation and settling ($HS^- + H_2S$)
HS^-	Water soluble ionized hydrogen sulfide
H_2S	Un-ionized hydrogen sulfide, calculated from dissolved sulfide, sample pH, and practical ionization constant of H_2S
Freely available sulfide	Dissolved sulfide plus sulfide weakly associated with organics
Acid-soluble metallic sulfides	Metal sulfides soluble in acid solution
Organic reduced sulfide compounds	Organic compounds containing sulfur, commonly MeSH, DMS, DMDS, DMTS

The preservation technique recommended in *Standard Methods* and in EPA Method 376.1 for sulfide involves addition of a basic zinc acetate solution (APHA 2005; USEPA 1978). These methods analyze samples after acidification and therefore assess total sulfide. NCASI RSC-02.01 and RSC-02.02 utilize a similar preservation and analysis approach, also providing a measurement of total sulfide concentration.

The majority of methods utilized for the detection of organic sulfur compounds (MeSH, DMS, DMDS, and DMTS) use gas chromatography with a sulfur selective detector. These methods differ mainly in the approach used to isolate and introduce the compounds to the GC. GC methods used to analyze RSCs in aqueous streams include solvent extraction (Andersson and Berfstrom 1969; Prakash and Murry 1976), sparging (Rayner, Murry, and Williams 1967; Caron and Kramer 1989; Saunders and Larson 1996; O'Conner and Genest 1997), headspace (Chai, Liu, and Zhu 2000; NCASI 2000), and direct injection (Bérubé, Parkinson, and Hall 1999). Solvent extraction methods suffer from poor sensitivity because a concentration step cannot be performed due to the volatility of RSCs. Multiple solvents may be needed to effectively extract all the compounds, and the solvents may interfere with GC analysis. Sparging methods are complicated, multi-step, time- and labor-intensive procedures. They require special glassware and gas handling equipment with gas phase calibrations. Headspace methods have been used for analysis of RSCs in black liquor (Chai, Dhasmana, and Zhu 1998) and are currently under investigation by NCASI for application to wastewater samples.

NCASI used the direct aqueous injection approach for determination of total sulfide and ORSCs described by Bérubé, Parkinson, and Hall (1999) as the basis for development of Method RSC-02.01

(Gholson, Hoy, and Chambers 2002). Injection volume was minimized so less potential interferents entered the column, a cool injection port was applied to minimize the amount of water entering the column, and the injection sleeve was packed with glass wool to prevent nonvolatile components from getting onto the column. A sensitive detector, the pulse flame photometric detector (PFPD), was required to achieve the desired detection limits using a small injection volume (Cheskis, Atar, and Amirav 1993). The PFPD eliminated the flame-out problem associated with direct aqueous injections, as the flame is reignited three times per second. Because of the pulsed flame, the sample signal can be delayed to minimize the contribution of carbon to the sulfur signal, resulting in both better selectivity and a higher signal to noise ratio. The PFPD yields a sensitivity of 1 pg S for DMS, an order of magnitude increase in sensitivity over a flame photometric detector. A capillary column was used with the PFPD, increasing sensitivity by decreasing peak width. NCASI has analyzed a variety of samples from WWTPs since the method's initial development and evaluation, and in the process has revised the method to enhance its performance.

2.0 REVISION OF NCASI METHOD RSC-02.01 (RSC-02.02)

This section provides information regarding the revision of NCASI Method RSC-02.01 and a summary of the quality assurance and quality control data acquired during the past several years for the original method (NCASI 2002; Gholson, Hoy, and Chambers 2002) and its recent revision, RSC-02.02 (Appendix A). Major revisions include a section describing the forms of sulfide assessed using the method; sections on precautions required to deactivate metal surfaces and clean the injection port; procedures to address excessive peak broadening; changes to the lower calibration limit of the method (increased from ~10 to ~20 µg S/L); procedures to verify the concentration of the sulfide standard; additional instructions regarding preparation of the zinc acetate preservation solution; surrogate recovery procedures and criteria; and revisions to the quality control criteria for calibration curves, daily calibration verifications, matrix spike recoveries, and duplicate precision.

2.1 Method Summary

Method RSC-02.02 is used to determine concentrations of total sulfide, MeSH, DMS, DMDS, and DMTS in wastewaters from pulp and paper mills. RSCs are measured by direct aqueous injection GC/PFPD. The concentration of sulfide measured using this method represents the total amount of sulfide in the sample that is volatile at pH 2.5. It is believed that this includes all freely dissolved sulfide plus sulfide weakly associated with either dissolved organic matter or certain transition metals. If the native pH of a sample is greater than 2.5, the actual sulfide concentration in solution might be less than the concentration measured by this method.

The method utilizes separate injections for total sulfide and ORSCs. This is required in order to preserve the compounds effectively. Samples collected for total sulfide analyses are preserved by the addition of 39.8 mg of zinc acetate dehydrate and ~0.0005 equivalents of NaOH per 40 mL (VOA vial) of sample (pH >10). Preservation of MeSH, DMS, DMDS, and DMTS involves addition of 120 mg of ascorbic acid and adjustment to pH <2.5 using a 1:3 phosphoric acid solution. Prior to analysis a portion of the sample is transferred to an autosampler vial in the laboratory, acidified to pH <2.5 (total sulfide), and spiked with internal standard (thiophene) and a surrogate recovery standard (thioanisole). Samples are analyzed via GC/PFPD by injecting a 1 µL sample in split mode onto a GC equipped with a Crossbond® 6% cyanopropylphenyl/ 94% dimethyl polysiloxane fused silica capillary column (J&W DB-624, 30 m x 0.25 mm i.d. with 1.4 µm film). The injection port is cleaned and the injection port liner is changed prior to each sample set to avoid problems associated with buildup of contaminants in the system, especially ones that generate a sulfur dioxide artifact peak that can interfere with quantitation of methyl mercaptan. RSCs are identified by comparing their relative retention times with the relative retention times of the internal standard using a multipoint

calibration covering the range from ~20 to 1000 µg S/L. Samples with concentrations above the highest calibration point are diluted prior to analysis. The criterion for acceptable linearity is a mean absolute percent error (MAPE) for the curve of ≤20%. The results of the calibration curve for each compound are either fitted to a quadratic equation or described by an average relative response factor, depending on which meets the MAPE criterion.

The quality of the data generated using this method is assured by calibration checks, daily blank assessments, sample duplicate analyses, and matrix spiked samples with each set of samples analyzed on a given day. In addition, surrogate spike recoveries are determined within each matrix tested. The resolution of the separation of DMS and CS_2 is determined periodically to assure that chromatography is consistent.

2.2 Mill Wastewater Treatment Plants Sampled

A variety of samples collected from WWTPs were utilized during validation and application of this method. Table 2.1 shows information regarding mill furnish, process type, condensate management, and WWTP type.

Table 2.1 Mill Wastewater Treatment Plants Sampled

Mill Code	Furnish[a]	Process Type[b]	Condensate Management	WWTP[c]
A	SW	kraft	hard piping	ASB
B	SW, deink	GW, TMP, recycle	NA	AS/ASB
C	SW, OCC	kraft	hard piping	ASB
D	SW	kraft, dissolving kraft	hard piping	ASB
E	SW, OCC	kraft, recycle	steam stripping	ASB
F	SW/HW, OCC	kraft, recycle	steam stripping	ASB
G	SW, HW	kraft	steam stripping	ASB
H	SW, HW, deink	kraft, recycle	steam stripping/hard piping	ASB/AS
I	SW	kraft	steam stripping/hard piping	ASB
J	HW, SW, OCC	kraft, recycle, NSSC	hard piping	ASB
K	HW, SW	kraft	hard piping	ASB
L	SW, deink	TMP, recycle	NA	AS
M	HW, OCC	NSSC, recycle	hard piping	ASB/AS
N	HW/SW	kraft	hard piping	AS
O	SW	kraft	steam stripping	ASB
P	SW	kraft	steam stripping	ASB
Q	SW/HW, OCC	kraft, recycle	steam stripping	ASB
R	SW/HW	kraft	steam stripping	ASB
S	SW/HW	kraft	steam stripping	ASB
T	SW/HW	kraft	hard piping	ASB
U	SW/HW	kraft	NA	ASB
V	SW/HW	kraft	steam stripping	AS/ASB

[a] HW = hardwood; SW = softwood; OCC = old corrugated containers
[b] GW = groundwood; TMP = thermo-mechanical pulping; NSSC = neutral sulfite semi-chemical
[c] AS = activated sludge; ASB = aeration stabilization basin
NA = not applicable

3.0 METHOD VALIDATION

Preparation and preservation of the standards utilized in this method have proven to be critical steps. During initial method development, primary standards of MeSH, DMS, DMDS, and DMTS were gravimetrically prepared from neat compounds to a concentration of approximately 1000 µg S/mL in methanol. The total sulfide standard was prepared from sodium sulfide nonahydrate in purged deionized water. Because the PFPD has an equal molar response for sulfur, standards were prepared to have equal quantities of sulfur. Primary stocks were utilized to prepare a five-point calibration curve at concentrations of ~20, 50, 200, 500, and 1000 µg S/L. An independent check standard containing MeSH, DMS, and DMDS was obtained from Crescent Chemicals. The recoveries of an aliquot of this standard diluted to a concentration of 500 µg/mL and analyzed four times over a six-day period provide an indication of the validity of the calibration stocks. The analyses of the independent check standards yielded average recoveries and RSDs, respectively, of 85.5% and 11.1% for MeSH, 119% and 6.9% for DMS, and 112% and 10.7% for DMDS, verifying that calibration standards and independent check standards were in good agreement for these compounds. Confirmation of the sulfide standard is more complex due to the instability of the standards.

3.1 Sulfide Standard Concentration

Standards of unpreserved sulfide solutions (500 µg S/L) were found to be unstable, losing over 20% after 24 hours, depending on the handling of the stock solution (Figure 3.1).

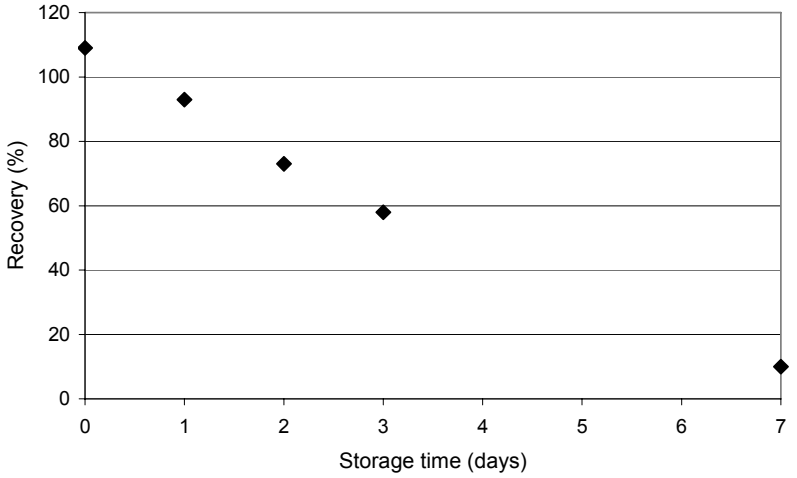


Figure 3.1 Unpreserved Sodium Sulfide Standard Recovery over Storage Time

To increase stability of the sulfide standard, it was prepared at a concentration of 500 µg S/mL in a solution of 0.03 molar zinc acetate adjusted to pH 10 with 1N sodium hydroxide solution. This standard was a dispersed colloid of a zinc bisulfide complex which has been found to be stable to oxidation over a period of several months when stored at 4°C. When using the preserved stock standard, care must be taken to allow it to come to room temperature and to mix it thoroughly prior to removing an aliquot for use. Because this solution is a colloidal suspension, verifications of reproducibility of the standard concentration were performed by analyzing three replicates from the vial. Reproducibility and stability were also verified for each set of samples by conducting a calibration verification and calculating the percent recovery. The sulfide standard utilized in the laboratory was periodically verified for concentration accuracy using an independent laboratory. Verification included confirmation of the standard concentration using three different analytical techniques: EPA Method 376.1, sulfide by titration (USEPA 1978); EPA Method 376.2, sulfide by colorimetry (methylene blue) (USEPA 1997); and peroxide oxidation followed by EPA Method 300 (USEPA 1993). Oxidation converts the sulfide in the standard to sulfate, which is assessed by ion chromatography. Results obtained for the sulfide standard verifications are summarized in Table 3.1. They indicate good agreement with the gravimetrically calculated concentration of the total sulfide standard.

Table 3.1 Confirmation of Total Sulfide Standard Concentration Using Three Independent Methods

Gravimetric (mg S/L)	EPA Method 376.1 (mg S/L)	EPA Method 376.2 (mg S/L)	EPA Method 300 (mg S/L)	Average (mg S/L)
197.9	193	204	188	195
149.1	156	158	136	150

3.2 Instrument Calibration

To establish the calibration function for the method, a multipoint internal standard calibration covering the operating range of the method (~20 to 1000 µg S/L) was performed (Appendix A, Section 10.2). The best quadratic fit was assessed by plotting the response ratio of each compound versus the ratio of the standard concentration versus the internal standard. Curve-fitting software (Agilent Chemstation) was utilized to find the best quadratic fit for the data. Alternatively, the

average response factors for each compound were calculated and evaluated to determine which approach best met the calibration criteria based on a MAPE of <20% for each compound. The MAPE calculation is shown in Equation 1. This approach is utilized to evaluate the fit between model predictions and measured values. In this case the prediction determined using a quadratic fit curve was compared to the measured concentrations for the target compounds determined at each concentration level of a five-point calibration curve. The MAPE data for eighteen calibration curves analyzed over a period of five years are summarized in Table 3.2. Outliers were determined using a Grubbs test, and one value for total sulfide was removed.

$$MAPE = \frac{\sum \left| \frac{C_{cal} - C}{C_{cal}} \right| * 100}{n} \qquad \text{(Equation 1)}$$

where: MAPE is the mean absolute percent error
C_{cal} is the concentration in the calibration standard
C is the concentration measured for the calibration level
n is the number of calibration levels

Table 3.2 Mean Absolute Percent Error (MAPE) Calculations for Calibration Curves

Compound	MAPE Average	Standard Deviation	Range of MAPEs	n
Total sulfide	11.4	5.42	3.20 - 25.5	17
MeSH	10.0	5.36	4.02 - 21.0	18
DMS	10.6	4.50	3.30 - 19.2	18
DMDS	9.78	4.35	3.40 - 16.8	18
DMTS	9.85	4.28	2.20 - 16.6	18

These data indicate good agreement between the concentrations determined using a quadratic fit equation for the calibration curve and the gravimetrically determined concentrations of the standards.

3.3 Ongoing Calibration Verification

A calibration verification or ongoing recovery standard was assessed daily with each set of samples analyzed (n <20). This check was conducted at a concentration of ~200 µg S/L by spiking 1.8 mL of purged Barnstead deionized water with the target analytes and calculating the recovery of the spike following acidification of the samples with 1:3 phosphoric acid and direct injection on the GC/PFPD under the conditions described in Appendix A, Section 11.0.

Results of the calibration verifications performed during this study are summarized in Table 3.3. The data were examined for the presence of outliers using a Grubbs test and none were found. Table 3.3 contains the average percent recovery determined for 94 calibration verifications conducted in conjunction with total sulfide analyses and 42 calibration verifications conducted in conjunction with ORSC analyses. The pooled relative standard deviation (RSD) of the recoveries and the range of recoveries observed are provided. Average calibration verification recoveries ranged from 95 to 111% across all target analytes. Pooled RSDs for the recoveries ranged from 8.3 to 11.5%. Calibration verification criteria for the method were established from these data using the standard EPA calculations of warning and action limits (IDQTF 2005). Warning limits are the average recovery ±2 times the SD of recoveries, and action limits are the average recovery ±3 times the SD of recoveries. Warning limits for the target analytes ranged from 74.7 to 129%.

Table 3.3 Daily Calibration Verification Summary for NCASI Method RSC-02.02

Parameter	Total Sulfide	MeSH	DMS	DMDS	DMTS
Average % recovery	106	95	100	111	102
Pooled RSD of recoveries, %	11.2	10.6	10.5	8.3	11.5
Range of % recoveries	81.0 - 130	72.0 - 121	83.0 - 119	94.0 - 131	85.0 - 134
Warning limits	81.0 - 129	74.7 - 115	79.3 - 122	92.5 - 129	78.5 - 126
Action limits	70.1 - 141	64.7 - 125	68.7 - 132	83.3 - 138	66.7 - 137
n	94	42	42	42	42

3.4 Method Detection Limit

The method detection limit (MDL) was calculated using the EPA approach described in 40 CFR Part 136 Appendix B (Federal Register 1984). A sample of final effluent from an unbleached kraft mill was stored without preservation and used as a matrix for the MDL experiment after the sulfide concentration had dropped to less than 50 µg S/L. The sample was fortified with the ORSCs at the concentrations listed in Table 3.4. The sample was analyzed ten times, with the results shown in Table 3.4 (experiment 1). Except for total sulfide, the MDLs obtained were below the calibration range and an analysis of a standard at these levels failed to provide peaks greater than three times the baseline noise. The experiment was repeated to confirm these findings and yielded similar results (experiment 2). This illustrates the potential for the EPA MDL method to underpredict the concentration at which analytes can be detected. Until a better estimate of the MDL can be made, the lower level of the calibration curve is a safe value to use as a detection limit.

Table 3.4 Method Detection Limit Study Findings

Compound	Mean Concentration (µg S/L)[a]	RSD (%)	Experiment 1 MDL (µg S/L)	Experiment 2 MDL (µg S/L)
Total sulfide	52.2	21.8	32.0	34.0
MeSH	23.4	10.0	6.6	9.9
DMS	14.7	12.5	5.2	10.1
DMDS	22.9	12.1	5.9	5.6
DMTS	22.5	5.8	3.8	5.0

[a] results for n = 10 replicates

3.5 Analytical Method Blanks

A blank was analyzed with each sample set to assess background levels of the target analytes in purged Barnstead deionized water, the spiking solutions of internal standard and surrogate, and background concentrations that may be released from the GC system upon acidification. Blanks were prepared by placing a 1.8 mL aliquot of purged Barnstead deionized water in an autosampler vial and spiking it with the appropriate amount of internal standard and surrogate compound. The solution was acidified (pH <2.5) by addition of 15 to 20 µL of 1:3 phosphoric acid and was injected onto the GC/PFPD. None of the target analytes were detected in the analytical method blanks during determination of total sulfide (n=94) or ORSCs (n=42).

3.6 Precision and Accuracy

3.6.1 *Surrogate Recovery*

Each sample was spiked with a surrogate (thioanisole), and its recovery was determined. These data provide an assessment of the method's accuracy in each sample matrix measured. A summary of the surrogate recovery data is provided in Table 3.5.

Table 3.5 Surrogate Recovery Summary

Parameter	Thioanisole Results
Average % recovery	106
Pooled RSD of recoveries	6.8
Range of % recoveries	73.0 - 131
Warning limits	92.0 - 121
Action limits	85.0 - 128
n	1077

To evaluate the impact of sample matrix on surrogate recovery, the data were examined by plotting the recoveries obtained in samples collected from primary clarifiers, the front portions of aerated stabilization basins (ASBs), midpoints of ASBs, final effluents, and hard piped condensates. An additional category called "other" included all samples collected at sites such as process sewers and belt press filtrates. Surrogate recoveries from total sulfide and ORSCs are summarized in Figures 3.2 and 3.3, respectively, in the form of box-and-whisker plots. Each plot provides a central box that covers the middle 50% of the data; the sides of the box are the lower and upper quartiles, and the horizontal line drawn through the box is the median. The whiskers extend to the lower and upper values of the data (range), and the single point (+) is the mean. Values that fall beyond the whiskers but within three interquartile ranges are suspected outliers and are plotted as small boxes. A Grubbs test was utilized to determine any outliers (n=2), and they were removed from the data set prior to graphing.

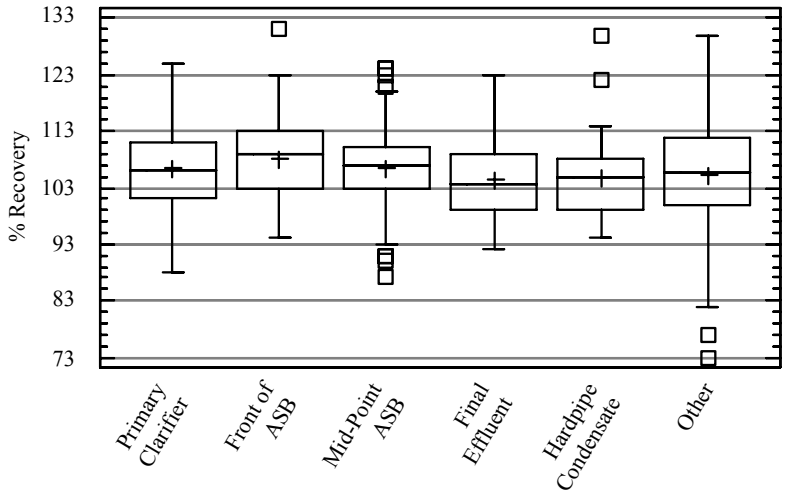


Figure 3.2 Surrogate Recoveries of Total Sulfide in Wastewater Treatment Plant Matrices

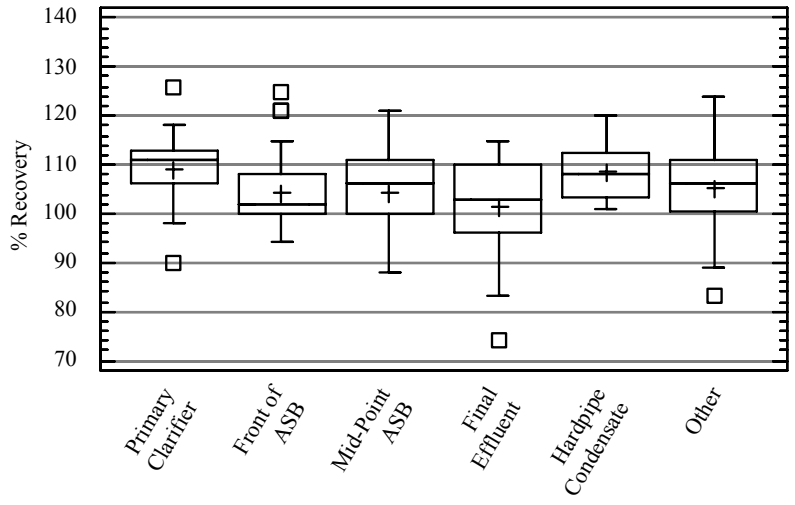


Figure 3.3 Surrogate Recoveries of Organic Reduced Sulfur Compounds in Wastewater Treatment Plant Matrices

3.6.2 *Accuracy in a Matrix: Matrix Spike Recovery*

Accuracy was assessed with each sample set analyzed by fortifying a sample with the target analytes at concentrations one to five times the native concentration. Recoveries of the spiked target compounds were calculated for each experiment and a summary of the data is provided in Table 3.6. A Grubbs test was utilized to determine any outliers (n=1), and they were removed from the data set prior to summarizing the data and performing subsequent calculations. Average matrix spike recoveries ranged from 93 to 112%, with a pooled relative standard deviation ranging from 11.7 to 24.1% depending on the target compound. These data were utilized to calculate matrix spike recovery criteria for Method RSC-02.02 by calculating the warning and action limits listed in the table (IDQTF 2005).

Table 3.6 Matrix Spike Recovery Summary

Parameter	Total Sulfide	MeSH	DMS	DMDS	DMTS
Average % recovery	93	106	102	112	96
Pooled RSD of recoveries	20.7	20.0	11.7	16.5	24.1
Range of % recoveries	43.0 - 124	38.0 - 172	77.9 - 131	75.2 - 158	44.7 - 143
Warning limits, %	54.7 - 132	74.7 - 115	78.3 - 126	75.1 - 149	50.1 - 143
Action limits, %	35.4 - 151	42.1 - 169	66.3 - 138	56.5 - 168	26.8 - 166
n	70	33	34	34	34

3.6.3 *Precision in a Matrix: Duplicate Analyses*

Method precision was evaluated with each sample set by analyzing a sample in duplicate and determining the relative percent difference (RPD) between the sample and duplicate concentrations. Precision data were assessed by pooling the RPDs observed between duplicate sets. Table 3.7 is a summary of these data as well as the calculated upper warning and action limits for method precision. The average pooled RPDs ranged from 2.1 to 5.3%, indicating good precision for the method. The

highest variability was observed for total sulfide and methyl mercaptan, as anticipated, as these compounds are the most unstable and reactive of the target compounds.

Table 3.7 Precision in Wastewater Treatment Plant Matrices

Parameter	Total Sulfide	MeSH	DMS	DMDS	DMTS
Average pooled RPD%	5.3	5.2	2.8	2.1	3.9
Range of RPDs%	0.2 - 17	0.6 - 20	0.2 - 6.0	0.1 - 8.0	<0.02 - 11
Warning limits, %	13.1	16.3	6.6	6.3	9.8
Action limits, %	16.9	21.9	8.5	8.4	12.8
n[a]	69	20	17	17	14

[a] n is dependent on compounds detected in native samples utilized during these assessments

3.7 Sample Preservation and Stability

3.7.1 *Initial Experiments to Assess the Stability of Reduced Sulfur Compounds using Various Preservation Techniques*

Due to the reactivity of RSCs, which can react with surfaces, volatilize, oxidize, or be biochemically transformed, sample stability is often one of the major problems encountered. Gholson, Hoy, and Chambers (2002) conducted studies to address surface reactivity by deactivating sampling glassware with acid and trimethylsilozanes, collecting samples using standard volatile organic methods (no-splash sampling, zero headspace storage, and refrigeration), adjusting sample pH to <2.5 or >10 to control bioreactivity, and using antioxidants to control oxidation. Experiments to control oxidation included an investigation of the use of sodium thiosulfate, ascorbic acid, sodium bisulfite, glutathione, and pyrogallol. Results indicated that sodium thiosulfate and sodium bisulfite were incompatible with the analytical method, and chromatographic interferences were encountered with glutathione. Ascorbic acid was found to be more effective than pyrogallol in preserving MeSH and sulfide. These findings indicated that reducing pH using phosphoric acid and ascorbic acid improved stability for MeSH, DMS, DMDS, and DMTS in most matrices, but stability of sulfide was still lacking in several matrices. Additional studies were conducted to improve the stability of total sulfide using a zinc acetate solution to form a stable complex of zinc sulfide.

3.7.2 *Sample Storage Stability*

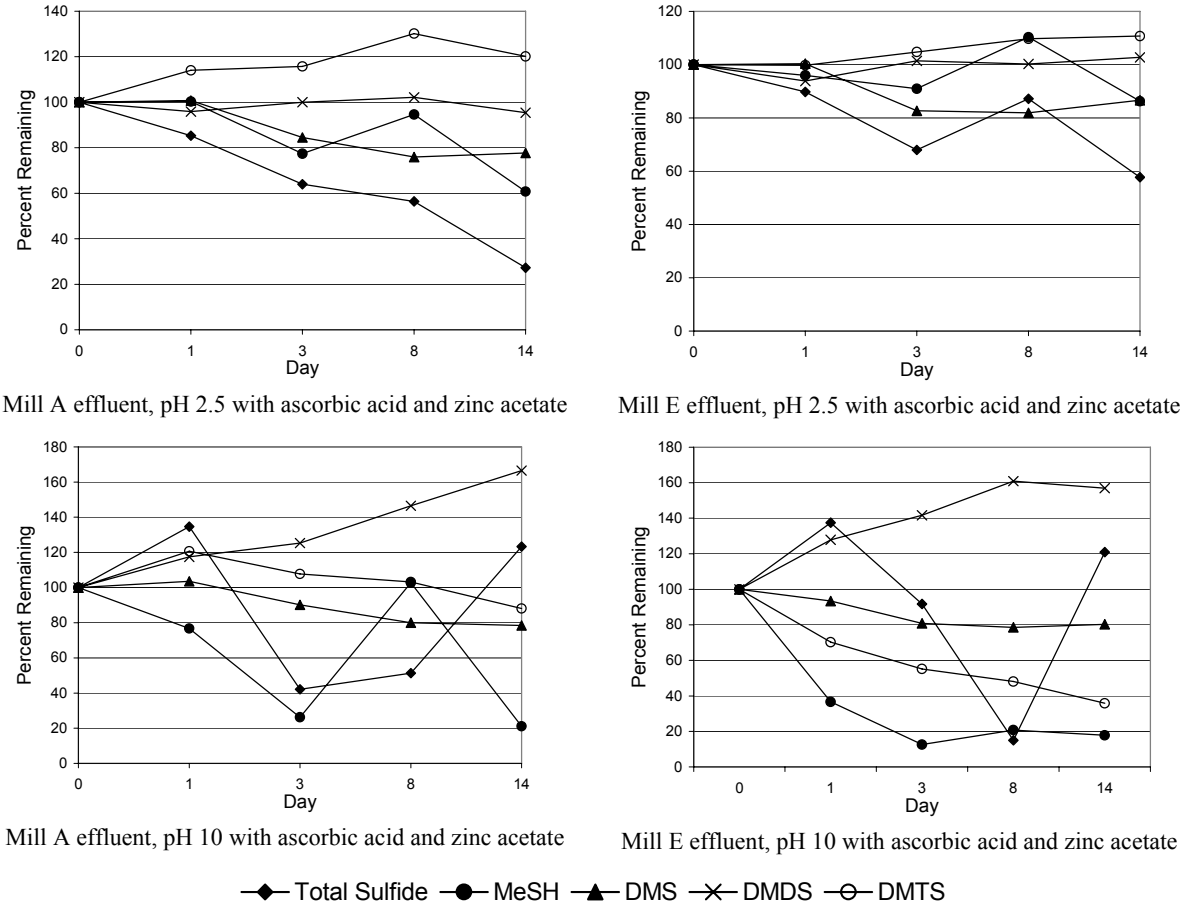
Experiments were conducted to investigate the storage stability of total sulfide in effluent samples from Mills A and E (a bleached and an unbleached kraft mill, respectively) when preserved using a solution of ascorbic acid and zinc acetate at pH 10 and at pH 2.5 over a period of 14 days. Aliquots of the various samples were analyzed in duplicate or triplicate on each day assessed (Appendix A, Section 11, acidification and direct injection on the GC/PFPD). The concentrations remaining in each aliquot on each day of testing were calculated and are shown in Figure 3.4.

These results indicate that ORSCs were stable (>~80% remaining) in solutions of ascorbic acid and zinc acetate at pH 2.5 out to 14 days in Mill E effluent and out to 8 days in Mill A effluent. The concentrations of sulfide remaining in solution dropped off over three days under similar conditions. The findings at pH 10 were more variable for sulfide, but the general trend for the ORSCs was decreasing after Day 3 for all but DMDS. This was probably due to oxidation of MeSH to DMDS in the matrix; thus as MeSH decreased DMDS increased.

To assess the impact of ascorbic acid versus zinc acetate the experiment was repeated using solutions of zinc acetate at pH 10 and 2.5 without the addition of ascorbic acid. Results are illustrated in Figure 3.5. When the percent of sulfide remaining dropped below 60%, one more experiment was conducted

to confirm this trend, and then further analyses were discontinued. At pH 2.5 this occurred between Day 0 and Day 1 in the effluents from Mills A and E, although in Mill E effluent the ORSCs appeared stable so further analyses were conducted out to Day 7. At pH 10 it was apparent after Day 1 that MeSH was not stabilized, but sulfide remained stable out to 16 days.

As illustrated in Figure 3.4, ascorbic acid at pH 2.5 stabilized ORSCs but not sulfide. Figure 3.5 illustrates stabilization of sulfide at pH 10 with zinc acetate, while methyl mercaptan is lost under those conditions. Based on these experiments, two preservation schemes were adopted for the NCASI RSC method: preservation at pH 2.5 with the addition of ascorbic acid to act as an antioxidant for stabilization of the ORSCs, and preservation at pH 10 with zinc acetate for stabilization of total sulfide. The effectiveness of this approach was further substantiated by the stability observed for the sulfide standard in zinc acetate at pH 10, as discussed in Section 3.1.



Mill A effluent, pH 2.5 with ascorbic acid and zinc acetate

Mill E effluent, pH 2.5 with ascorbic acid and zinc acetate

Mill A effluent, pH 10 with ascorbic acid and zinc acetate

Mill E effluent, pH 10 with ascorbic acid and zinc acetate

Figure 3.4 Reduced Sulfur Compound Percent Remaining at pH 2.5 and pH 10 Preservation with Zinc Acetate and Ascorbic Acid

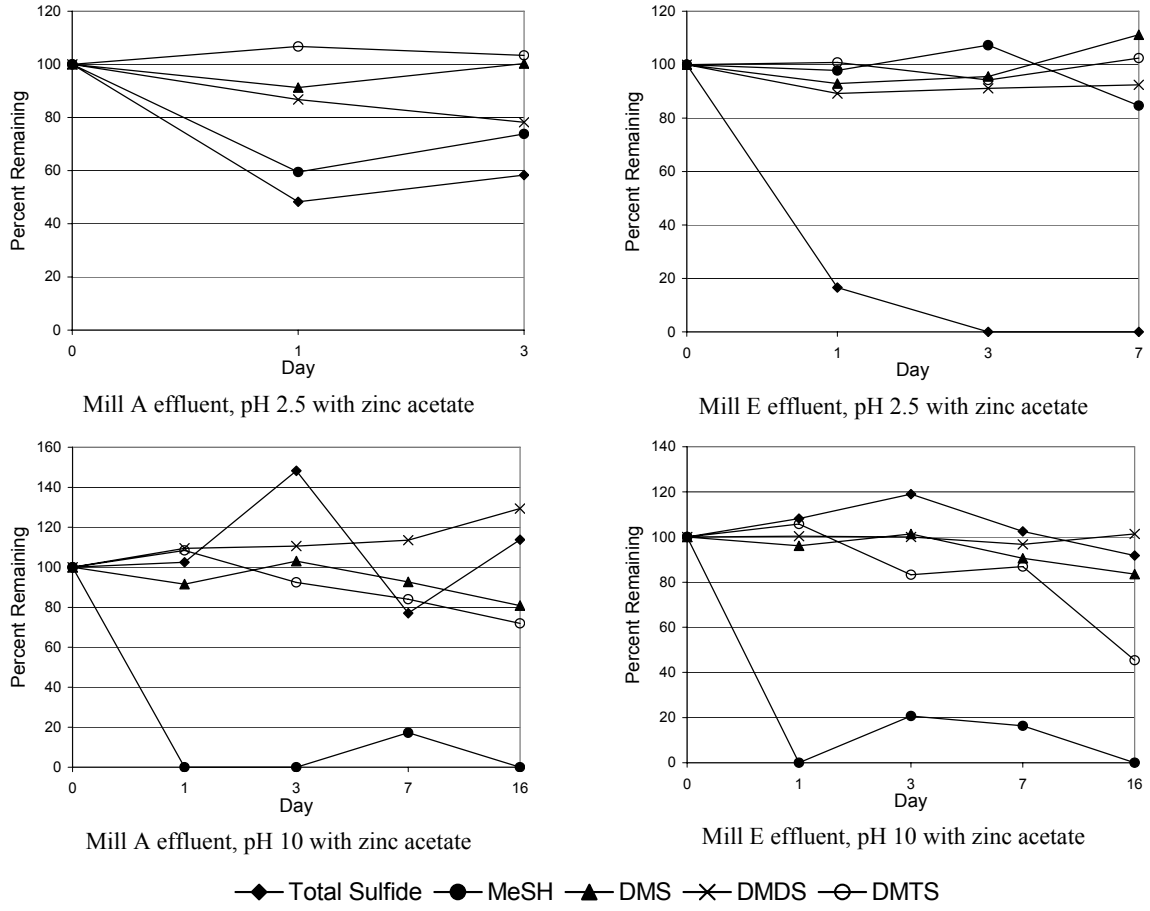


Figure 3.5 Reduced Sulfur Compound Percent Remaining at pH 2.5 and pH 10 Preservation with Zinc Acetate

3.7.3 *Ongoing Investigations of Sample Preservation and Stability*

While conducting a survey of the aqueous phase in a WWTP, wherein samples were split between the NCASI West Coast Regional Center and another laboratory, questions arose regarding differences in total sulfide concentrations reported using Method RSC-02.01. The method uses ascorbic acid at pH 2.5 for preservation of the ORSCs and zinc acetate at pH 10 for preservation of sulfide. The other laboratory utilized a different preservation for the target analytes that used zinc acetate and ascorbic acid adjusted to a final pH of 12.8 with sodium hydroxide solution. The concentration differences observed were most pronounced in samples from the front portion of the WWTP (settling pond outlet and the front portion of the ASB). Additional experiments were conducted to examine the difference in total sulfide concentrations due to preservation. NCASI staff collected samples at two mills in order to determine total sulfide concentrations in the native samples within 2 hours of collection. Samples were collected and aliquoted for preservation with zinc acetate at pH 10, ascorbic acid at pH 2.5, and zinc acetate plus ascorbic acid at pH >12. Unpreserved samples were also analyzed. Each of the differently preserved aliquots was analyzed on Days 0, 1, 4, or 5, and 14 using RSC-02.01 for total sulfide, yielding the results illustrated in Figures 3.6 and 3.7. As indicated in the figures, samples preserved with zinc acetate and ascorbic acid at pH >12 yielded the highest concentrations of total sulfide in all samples except Day 14 in the samples collected from Mill J. In all cases preservation

with zinc acetate at pH 10 or 12 in the sample collected at Mill A yielded higher concentrations than Day 0 unpreserved samples. This might indicate a loss of sulfide due to volatilization or oxidation in the Day 0 unpreserved sample. Alternatively, the high preservation pH may contribute to release of sulfide from other sulfur containing molecules in the matrix, yielding a false positive bias that is indicated by the trend of increasing concentrations over time for the samples preserved at pH 12.8. Samples preserved with ascorbic acid at pH 2.5 and unpreserved samples gave similar results on Days 0 and 1 in Mill A, while the ascorbic acid preserved sample concentrations were slightly lower in the Mill J samples. Concentrations of total sulfide in unpreserved samples dropped to nondetect on Day 4 or 5 in both sample matrices. Sulfide concentrations in samples preserved with ascorbic acid at pH 2 dropped steadily over the 14-day period in both matrices.

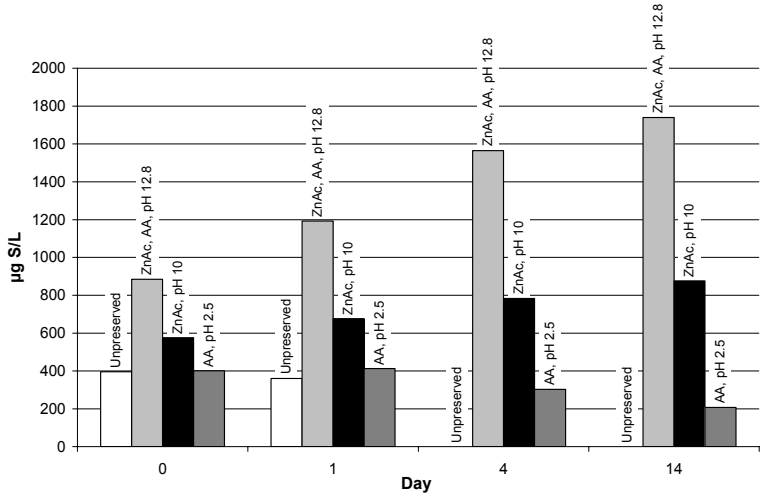


Figure 3.6 Mill A Preservation and Stability Results

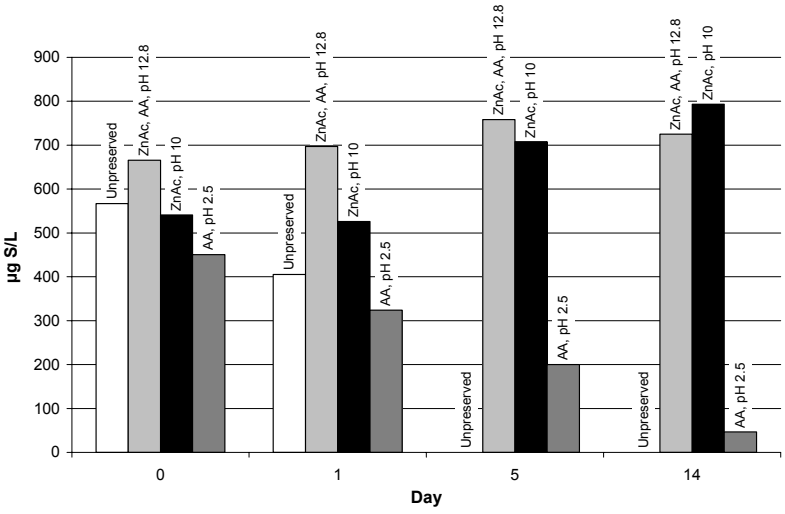


Figure 3.7 Mill J Preservation and Stability Results

Because preliminary experiments indicated that total sulfide concentrations increased with increasing pH (higher concentrations at pH 12 than at pH 10) and over time, further studies were done to address and understand this phenomenon. The objective of these studies was to evaluate the impact of sample preservation using zinc acetate over a pH range of 8 to 10 on total sulfide concentrations over a period of ~14 days. Samples for this work were collected from four mills (Mills I, P, Q, and S). Experimental work focused on samples collected at inlets to ASBs (primary clarifier outlet), front portions of ASBs, and midpoints of ASBs, as these sample matrices yielded the greatest differences in concentrations due to preservation pH observed in previous work. Unpreserved grab samples were collected by mill personnel and shipped to the NCASI West Coast Regional Center (WCRC) via overnight courier. Samples were collected using procedures for volatile organic compounds, were stored at 4°C, and were shipped to NCASI on ice. Comparisons were based on relative concentrations of total sulfide remaining in a sample starting from a designated Day 0 selected by the WCRC laboratory. Upon arrival at the laboratory, samples were screened to assess the amounts of base (1N NaOH) required to adjust a pH 8 zinc acetate stock to a pH that would allow the stock to be added to samples to achieve the desired pH of 8.0, 8.5, 9.0, 9.5, and 10.0 while adding the same amount of zinc acetate and the same volume of preservation stock (5 mL in a 40 mL VOA vial) to each sample, thus keeping the dilution factor constant. Samples were aliquoted in the laboratory in sets of three and adjusted to approximately pH 8, 8.5, 9, 9.5, and 10. An additional aliquot of unpreserved (UP) sample was also prepared. This provided a set of replicate samples to be analyzed on approximately Days 0, 2, 5 to 7, and 14. One replicate was analyzed using RSC-02.01 and the other was used to verify sample pH. This allowed verification that the targeted pH value was maintained while loss of sulfide was minimized. The actual day of analysis shifted slightly for the various sampling sets, depending on sample arrival at the laboratory.

Information regarding the samples utilized in this study are summarized in Table 2.1. Note that the initial pH of the sample from the primary clarifier at Mill S was 9 and that the Mill I samples were received at pH >8. The pHs of the designated aliquots were re-measured on each day of analysis to confirm that the adjusted pH level had been achieved and maintained over the 14 day period. Results of the preservation study are shown in Figure 3.8.

Different patterns were observed depending on the matrix and mill sampled. Unpreserved samples generally yielded the lowest concentrations of total sulfide on Day 0. Exceptions were observed in samples from the primary clarifier (initial pH (pH_i) 9.17, concentration 11.4 mg S/L) and the front of the ASB (pH_i 6.8, concentration 195 µg S/L) from Mill S, as well as from the midpoint of the ASB (pH_i 7.9, concentration 495 µg S/L) from Mill I. In those samples concentrations of total sulfide in unpreserved samples on Day 0 were similar to or higher than those in preserved samples. Stability of total sulfide in the unpreserved samples was poor, with 50% losses observed between Day 0 and Day 2 in a majority of the samples. Exceptions were observed in samples collected at the midpoint of the Mill I ASB and the front of the Mill S ASB. Based on these observations and previous studies, collection and shipment of unpreserved samples for total sulfide analyses using volatile sample collection techniques is not recommended.

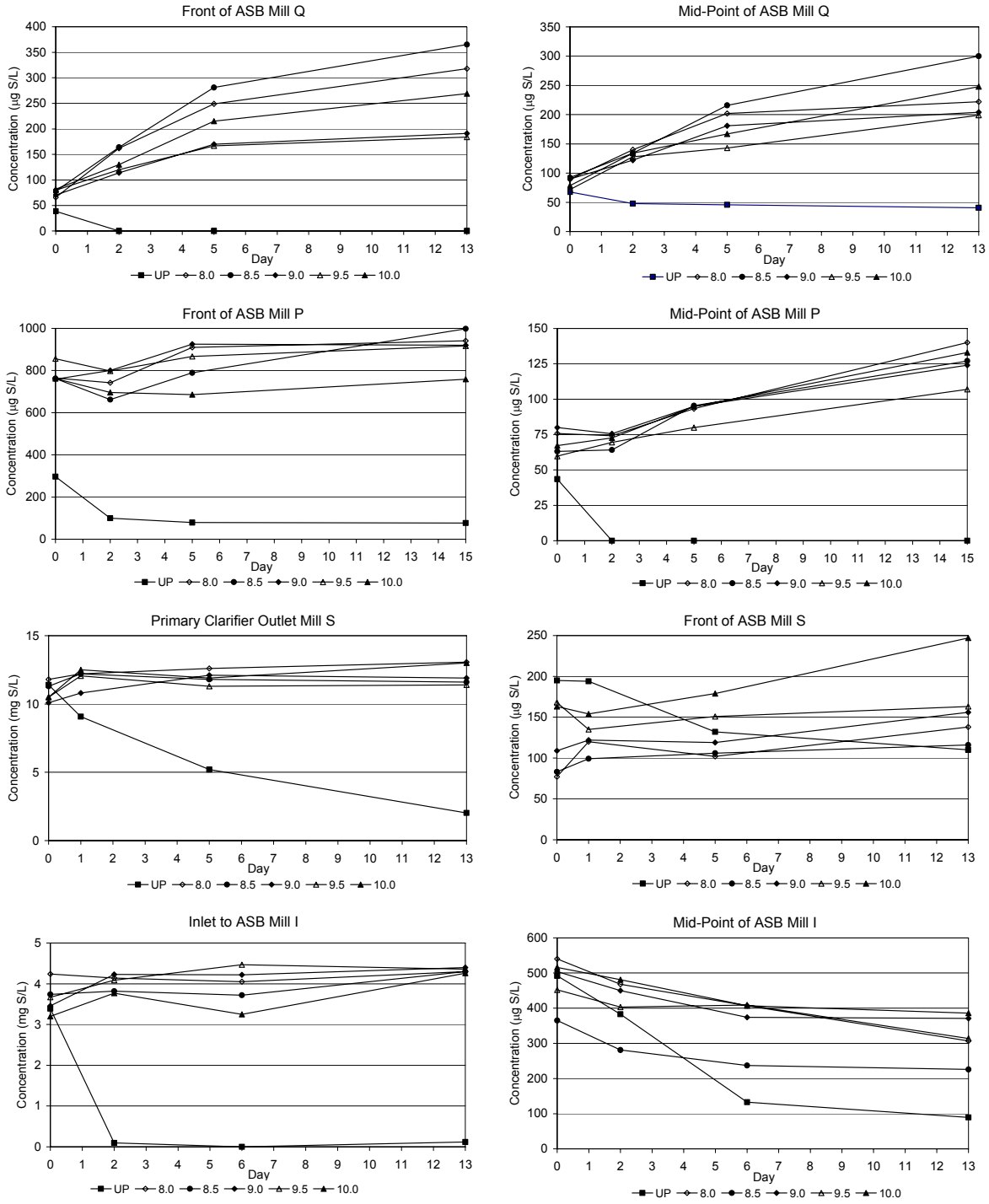


Figure 3.8 Preservation pH and Total Sulfide Concentrations over a 14-Day Period

Preservation pHs in the range of 8.0 to 10.0 yielded similar results for total sulfide. This suggest that the shift in total sulfide concentrations observed following addition of base and zinc acetate is matrix-specific and may be affected by two phenomena. The first involves a chemical pathway that results in an increased level of total sulfide immediately following addition of basic zinc acetate solution (possibly related to nucleophilic substitution or base catalyzed reactions). Another pathway occurs slowly over time to further increase total sulfide levels in some matrices. Investigations into the nature of these phenomena are still in progress. When biases for pH 9 and 10 results were plotted versus concentrations in the samples it was noted that the major bias occurred in samples with concentrations around 0.1 mg S/L (Figure 3.9). Therefore, samples with concentrations of sulfide below 0.1 mg S/L should be analyzed as soon as possible following collection.

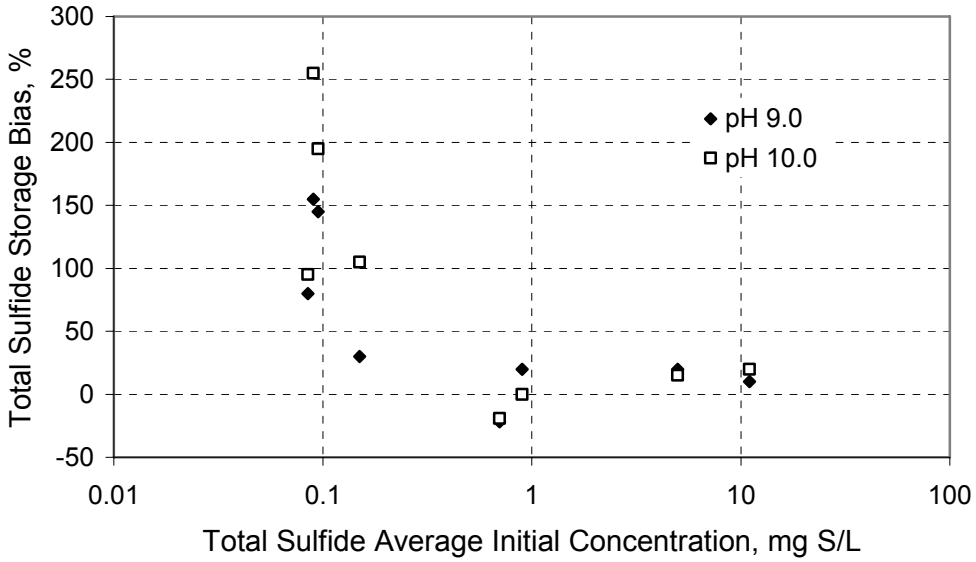


Figure 3.9 Total Sulfide Bias after Fourteen Days of Storage

Results of the preservation pH study indicate that in some matrices a change in native pH by the addition of basic zinc acetate preservation solution used in NCASI Methods RSC-02.01 and RSC-02.02 results in an increase in total sulfide concentrations measured. This increase was observed in samples collected from Mills Q and P at the fronts and midpoints of their ASBs. It was also observed in the sample collected from the midpoint of the ASB at Mill I. In the samples that demonstrated this increase it was observed at all pHs tested within the range of 8 to 10. This trend was observed in five of the ten samples tested.

Seven out of ten samples yielded increased total sulfide concentrations after one or two days of storage. Six out of ten samples yielded increased concentrations after five or six days. After 13 to 14 days, all samples tested to date (Mill I is not included) yielded increased total sulfide levels compared to unpreserved samples on Day 0. The magnitude of these changes appears to be matrix-specific and has not previously been observed in samples collected past the midpoint of the treatment system or prior to the front of the ASB. Therefore, the RSC-02.01 protocol is retained in RSC-02.02 for total sulfide analyses of samples requiring preservation and shipping, as limited benefits regarding alternative pHs of preservation were observed during this study. Investigations of alternative preservation schemes will continue, but based on the findings of this study and the volume of

literature available regarding sulfide preservation, the basic zinc acetate approach is the best available procedure at this time for samples requiring preservation or shipment.

Unpreserved samples lost total sulfide rapidly between Day 0 and Day 2 of analysis; therefore, analysis of unpreserved samples is not recommended if storage or shipping is required.

3.8 pH Adjustment Prior to Direct Injection

The objective of this study was to evaluate the impact of sample acidification following preservation with zinc acetate at pH 10 to release total sulfide for analysis. The experiment examined a range of pH adjustments prior to direct injection of total sulfide standards preserved using zinc acetate at pH 10 as specified in RSC-02.01 and RSC-02.02. In order to free sulfide bonds with zinc prior to direct injection onto the GC, samples were acidified to pH 2.0 to 2.5. This adjustment can also free sulfides associated with other metals and organics in the matrix.

Results of injection pH experiments are summarized in Table 3.8. The data indicate that in order to obtain recovery of the zinc preserved sulfide standard the pH of the sample must be adjusted to below pH 4 prior to injection. At pH 6, 0% recovery was observed. The post acidic injections were made in an effort to free any sulfide trapped in the injection port in the form of zinc sulfide. The first acidic injection following the pH 6 injection yielded additional sulfide. The second acidic injection also yielded additional sulfide, but to a smaller degree. Injection at pH 4 resulted in about 63% recovery of the sulfide standard, but further acidic injections did not result in additional detections of sulfide. This may be accounted for by losses expected to occur out of the split vent of the gas chromatograph during injection.

Table 3.8 Effects of Injection pH on Sulfide Standard Recovery

	pH 6 (% recovery)	pH 4 (% recovery)	pH 2.5 (% recovery)
Aliquot injected	0	63	96
First post acidic injection	30	0	0
Second post acidic injection	16	0	0

Experiments to investigate an optimum pH of adjustment prior to direct injection in order to free sulfide from the zinc preservative indicated that the currently used pH <2.5 is optimal for the greatest recovery of total sulfide.

3.9 NCASI Method RSC-02.02 Comments

As the data presented in the previous sections illustrate, NCASI Method RSC-02.02 is a precise (RSDs <12% in standards, RPDs <20% in samples matrices) and accurate (average recoveries >95%in standards, >93% in matrices) method for determination of RSCs in pulp and paper mill matrices. Sample preservation at pH 2.5 with ascorbic acid has proven effective for stabilization of ORSCs. Sample preservation at pH 10 with zinc acetate has proven effective in a majority of matrices assessed, although a high bias is sometimes observed in samples with initial concentrations below approximately 0.1 mg S/L. Preservation and storage stability studies indicated that >80% of the target compounds remained after a 14 day holding period using the preservation scheme in RSC-02.02 (Appendix A, Section 8.2).

Major challenges relate to the volatile and reactive nature of RSCs, which requires special attention to active sites on all syringes and instrumentation that will come in contact with samples. Instrument

maintenance is required on a daily basis, as well as careful sample handling to reduce losses following sample acidification (total sulfide).

4.0 METHOD APPLICATION

NCASI has used Methods RSC-02.01 and RSC-02.02 to survey WWTPs for total sulfide and ORSC levels in the aqueous phase. Many of the mills surveyed contacted NCASI for assistance in gathering data to address a variety of information needs; therefore, similar sampling sites were not always included at each mill. These data have been utilized by mills to help direct odor reduction efforts and provide insight regarding areas of the WWTP where increases (generation) and decreases (volatilization, oxidation, precipitation) of sulfide and ORSC concentrations are observed.

Many sulfur conversions can occur in the WWTP. Sulfide may be precipitated by metals as metal sulfides. It can become weakly associated with organics. Oxidation reactions, both chemical and biochemical, such as the conversion of methyl mercaptan to dimethyl disulfide and the oxidation of sulfide to sulfate, may take place. As the pH of the aqueous phase shifts, so does the equilibrium of sulfide. At higher pHs (>7.2) a majority of sulfide is water soluble (HS^-) and at lower pHs (<6.8) the sulfide is in gaseous form ($H_2S(g)$). In anaerobic areas sulfate maybe converted to sulfide by sulfate reducing bacteria. All these reactions contribute to a high level of variability with regard to sulfur forms and concentrations in the WWTP.

4.1 Results for Wastewater Treatment Plant Samples

Data for RSC concentrations in aqueous samples collected at the mills listed in Table 2.1 are summarized in Table 4.1. The data are not necessarily reflective of industry-wide RSC concentrations because the mills from which samples were collected were investigating odor sources and thus might represent a group with generally higher RSC levels. Sampling sites were variable, depending on each mill's WWTP configuration and information needs. Commonly sampled sites included output from the primary clarifier, front portion of the ASB or AS, midpoint of the ASB, and final effluent. Some samples required dilution prior to analysis in order to be within the working range of the method.

Results obtained on highly diluted samples have not been assessed or validated for this method; therefore, these data may be subject to error. The statistics in Table 4.1 (average, median, and SD) were calculated by substituting half the lower calibration limit (0.015 mg S/L for total sulfide, 10 µg S/L for ORSCs) for all target analytes with concentrations below the lower calibration limit of the method. A median value in the table near half the lower calibration limit indicates that the target analyte was not detected in a majority of samples assessed. Table 4.1 contains information from a total of 22 different units of operation. Figures showing concentrations of total sulfide and ORSCs in samples from the outlet of the primary clarifier, front of the ASB, and midpoint of the ASB can be found in Appendix B, Section B1. A majority of final effluent samples yielded concentrations below the lower calibration limit and were not graphed. The complete data set for the sampling sites assessed at each mill is provided in Appendix B, Section B2. These data characterize RSC concentrations encountered in aqueous samples from various locations in pulp and paper mill WWTPs.

Table 4.1 Reduced Sulfur Compound Summary for Mill Wastewater Treatment Plants

Parameter	Total Sulfide[a] (mg S/L)	MeSH[b] (µg S/L)	DMS[b] (µg S/L)	DMDS[b] (µg S/L)	DMTS[b] (µg S/L)
Primary clarifier outlet					
Range	<0.03 - 22.9	<20 - 3960	<20 - 2670	<20 - 2710	<20 - 470
Average	6.5	375	206	218	56
Median	3.5	38	66	22	10
SD[c]	7.1	847	502	489	98
n[d]	33	33	33	33	33
Front of ASB or AS					
Range	<0.03 - 21.6	<20 - 13900	<20 - 4680	<20 - 8410	<20 - 2500
Average	4.89	1795	682	1073	184
Median	2.95	60	68	68	18
SD	5.31	3346	1148	2178	463
n	32	32	32	32	32
Midpoint of ASB					
Range	<0.03 - 24.0	<20 - 2910	<20 - 2260	<20 - 2540	<20 - 353
Average	3.95	345	232	343	32.2
Median	0.29	<20	<20	<20	<20
SD	7.14	661	477	658	67
n	27	27	27	27	27
Final effluent					
Range	<0.03 - 0.46	<20 - 221	<20 - 59.8	<20 - 113	<20 - <20
Average	0.09	23.2	13.0	14.5	NA
Median	0.02	<20	<20	<20	NA
SD	0.12	39.7	10.2	19.1	NA
n	29	30	30	30	30

[a] half the lower calibration limit of 0.030 mg S/L (or 0.015 mg S/L) utilized for non-detects during these calculations

[b] half the lower calibration limit of 20 µg S/L (or 10 µg S/L) utilized for non-detects during these calculations

[c] standard deviation

[d] number of samples assessed

NA = not detected above lower calibration limit of the method

Figure 4.1 shows changes in concentrations of total sulfide observed in WWTPs as the wastewater progressed from primary clarification to final effluent. Some WWTPs were sampled more than once and are listed as the mill code followed by a roman numeral to indicate the different sampling dates. This graph includes different samplings that occurred at Mills C, D, J, K, O, S, and V to illustrate the variability observed at a given mill during distinct sampling episodes.

Figure 4.2 provides an indication of differences observed in ORSCs at various mills. This graph shows changes in methyl mercaptan concentrations through the WWTPs sampled. As indicated, methyl mercaptan concentrations at Mills C, D, and K increased following addition of hard piped condensates after primary clarification near the front portion of the ASB in those WWTPs.

Concentrations of DMS, DMDS, and DMTS yielded median results <68 µg S/L at all sampling locations surveyed at every mill. Trends in concentrations followed those observed for methyl mercaptan and were often linked to input of hard piped condensates to the WWTP.

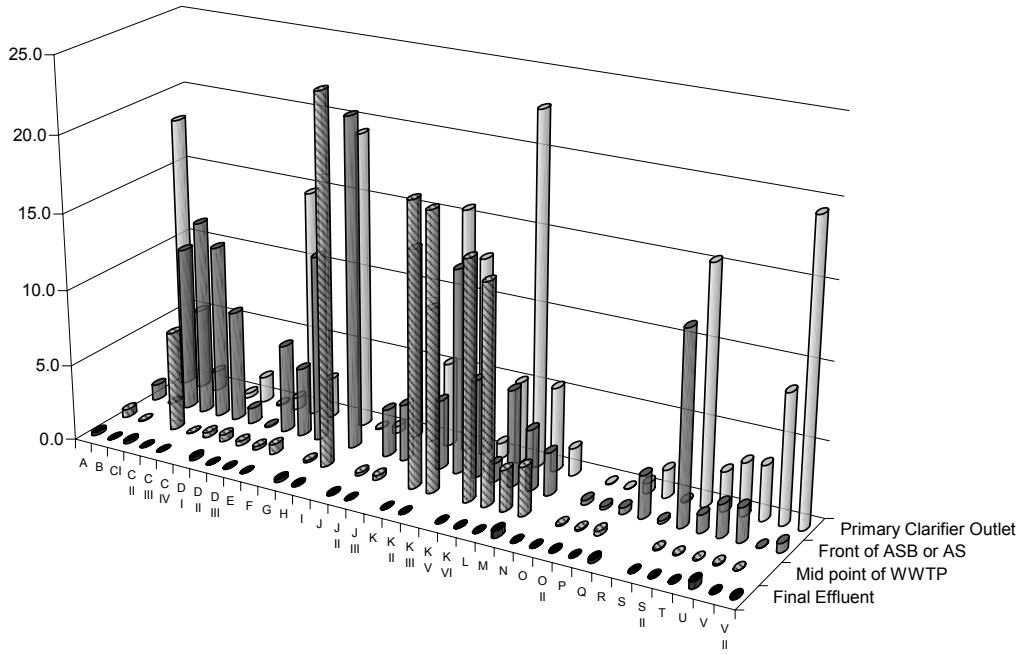


Figure 4.1 Total Sulfide Concentration (mg S/L) Changes in Wastewater Treatment Plants

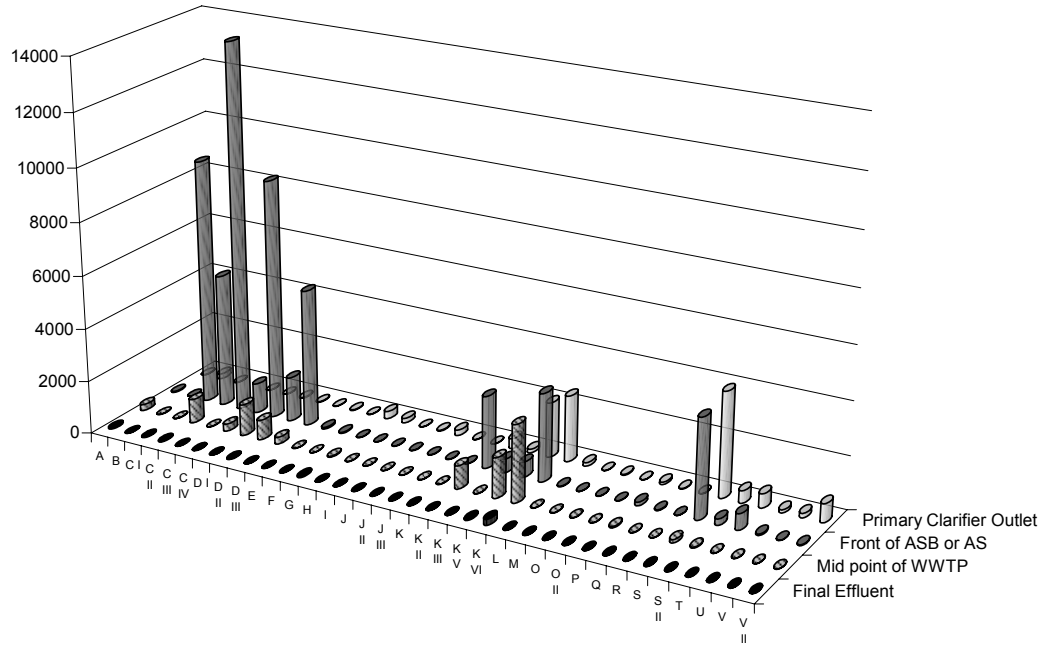


Figure 4.2 Methyl Mercaptan Concentration (μg S/L) Changes in Wastewater Treatment Plants

4.2 Matrix and Sampling Variability

In addition to the variability inherent in the method, pulp and paper mill matrix concentrations are expected to vary spatially (from site to site and sampling point to sampling point) and temporally (over time at the same mill). Temporal variability was assessed during application of the method to WWTP samples and results are presented in this section. Temporal variability would be anticipated to be higher at the front end of the WWTP (e.g., primary clarifier and first portion of the ASB), and decrease as effluent progresses through treatment. Therefore, several of the variability studies focused on samples from these front end locations. Several factors may impact matrix concentrations and variability, including pH, dissolved oxygen, volatilization, generation, and degradation. In addition, process variability occurring at each mill can impact concentrations of the target analytes in the WWTP. Experiments were conducted to assess matrix variability at various mills over the course of these studies. Study designs varied over the fours years during which this work was conducted and are described below with each data set. Results include variability due to the sampling process as a consequence of the reactivity and volatility of RSCs. Matrix-specific variability is represented more directly by results for DMS, which is more stable than the other RSCs.

The first experiment examined the variability of total sulfide concentrations at the ASB inlet of Mill D. Samples were collected every hour for seven hours and analyzed for total sulfide. Concentrations ranged from 2588 to 7729 µg S/L, with an average of 6052 µg S/L and a relative standard deviation of 31.2%. Further experiments at that site explored variability by collecting two to three samples per day for three days at the ASB inlet and one sample per day for three days at the ASB outlet. All target RSCs were evaluated during this experiment, yielding the results shown in Table 4.2.

Table 4.2 Variability in Mill D Aerated Stabilization Basin Sample Concentrations

	Total Sulfide	MeSH	DMS	DMDS	DMTS
ASB inlet					
Range (µg S/L)	312 - 4240	423 - 4030	481 - 1980	309 - 2280	86.3 - 2180
Average (µg S/L)	2568	2744	1117	948	996
RSD%	55	45	43	61	88
ASB outlet					
Range (µg S/L)	47.2 - 50.5	<20 - 28.4	27.1 - 33.8	132 - 170	<20
Average (µg S/L)	48.4	25.9	31.1	153	<20
RSD%	3.1	8.7	9.3	9.3	NA

NA = not applicable, concentration below lower calibration limit

The second study examined variability of the RSCs in an ASB at Mill T during one day. Samples were collected three times per day (AM, midday, PM) at the mix box prior to the ASB, the inlet of the ASB, and the outlet of the ASB. Results are summarized in Table 4.3.

The third experiment involved collection of samples three times per day for four days from the clarifier outlet at Mill J to assess variability in total sulfide concentrations. Concentrations ranged from 1150 to 6180 µg S/L, with an average of 3145 µg S/L and a relative standard deviation of 69.8%.

Table 4.3 Variability in Mill T Aerated Stabilization Basin Sample Concentrations

	Total Sulfide	MeSH	DMS	DMDS	DMTS
Mix Box Prior to ASB					
Range (µg S/L)	2600 - 4220	362 - 682	506 - 576	291 - 706	91.1- 183
Average (µg S/L)	3476.7	532	541	511	134
RSD%	23.5	30.3	6.5	40.8	34.4
ASB Inlet					
Range (µg S/L)	1610 - 2540	405 - 745	655 - 950	1120 - 2460	116 - 238
Average (µg S/L)	2160	605	838	1806	177
RSD%	22.6	29.4	19.1	37.1	34.4
ASB Outlet					
Range (µg S/L)			42.8 - 83.6	<20 - 180	
Average (µg S/L)	<30	<20	68.1	110.3	<20
RSD%	NA	NA	32.4	74.3	NA

NA = not applicable, concentration below lower calibration limit

The fourth experiment examined variability over a two day period at Mill K, with samples collected three times per day from the settling pond prior to the ASB (SPO), the front of ASB Pond 1 (FASBP1), and the outlet of ASB Pond 1 (OASBP1). Results are summarized in Table 4.4 and illustrated in Figure 4.3.

Table 4.4 Variability in Mill K Wastewater Treatment Plant Sample Concentrations

	Total Sulfide	MeSH	DMS	DMDS	DMTS
SPO					
Range (µg S/L)	1174 - 4056	130 - 361	182 - 219	195 - 440	45.0 - 79.5
Average (µg S/L)	3231	285	198	280	64.3
RSD%	33.2	31.7	3.9	29.7	17.7
FASBP1					
Range (µg S/L)	1208 - 4571	197 - 284	172 - 193	204 - 320	44.4 - 96.4
Average (µg S/L)	2727	235	186	260	64.8
RSD%	44.8	11.0	4.1	18.3	23.0
OASBP1					
Range (µg S/L)	9713 - 14022	555 - 868	218 - 459	30.5 - 84.5	22.4 - 53.7
Average (µg S/L)	11970	769	333	55.5	34.6
RSD%	11.6	15.4	22.2	35.1	33.2

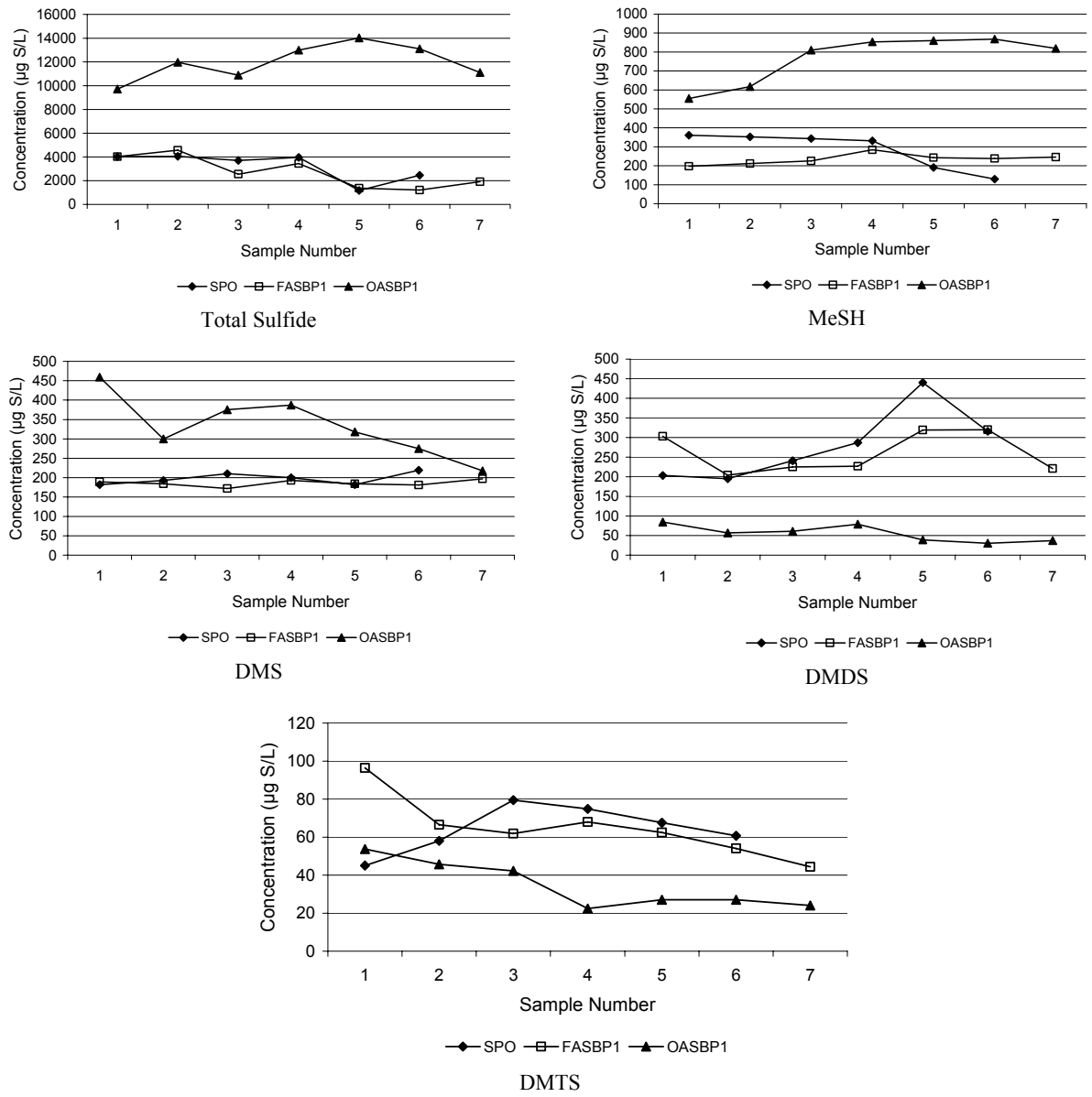


Figure 4.3 Variability in Mill K Wastewater Treatment Plant Samples

Additional studies were conducted at mill P over a four-day period. An average of three samples was collected at each site on each day of the study. The primary clarifier inlet and outlet and the ASB inlet and outlet were sampled, with the results reported in Table 4.5.

The level of variability observed during these samplings illustrates the complexity of assessing changes in RSC concentrations throughout a WWTP over time. Overall variability (RSD%) (Table 4.6) throughout the experiments described herein ranged from 3.1 to 81.4% with an average of 38.9% for total sulfide; from 8.7 to 46.7% with an average of 29.8% for MeSH; from 3.9 to 59.1% with an average of 20.6% for DMS; from 9.3 to 61.0% with an average of 34.2% for DMDS; and from 17.7 to 88.0% with an average of 41.0% for DMTS. This variability may be influenced by matrix,

sampling method, and analytical variability, which was determined to be less than 5.3% for all target analytes (Section 3.6.3).

Table 4.5 Variability in Mill P Wastewater Treatment Plant Sample Concentrations

	Total Sulfide	MeSH	DMS	DMDS	DMTS
Primary clarifier inlet					
Range (µg S/L)	213 - 853	31.5 - 93.7	29 - 46.9	751 - 1120	<20 - 44.1
Average (µg S/L)	526	56.0	37.0	840	22.0
RSD%	39.9	34.1	16.1	13.4	43.0
Primary clarifier outlet					
Range (µg S/L)	<30 - 1080	21.8 - 141	24.0 - 44.4	152 - 665	24.7 - 184
Average (µg S/L)	637	86	34	431	94
RSD%	64.7	46.7	22.0	42.5	51.6
ASB inlet					
Range (µg S/L)	<30 - 1020	62.6 - 232	23.1 - 114	73.3 - 465	20.7 - 73.3
Average (µg S/L)	417	134	42	217	43.0
RSD%	81.4	46.0	59.1	57.7	44.0
ASB outlet					
Range (µg S/L)	197 - 466	9.5 - 96.2	22 - 38	<20 - 20.7	<20
Average (µg S/L)	290	49.0	29	20.7	NA
RSD%	32.8	29.5	21.1	31.2	NA

NA = not applicable, concentration below lower calibration limit

Table 4.6 Matrix and Sampling Variability Summary (RSD%)

	Total Sulfide	MeSH	DMS	DMDS	DMTS
Mill D					
ASB inlet	31.2 and 55	45	43	61	88
ASB outlet	3.1	8.7	9.3	9.3	NA
Mill T					
Mix box to ASB	23.5	30.3	6.5	40.8	34.4
ASB inlet	22.6	29.4	19.1	37.1	34.4
ASB outlet	NA	NA	NA	NA	NA
Mill J					
Primary clarifier outlet	69.8				
Mill C					
Setting pond outlet	33.2	31.7	3.9	29.7	17.7
ASB inlet pond 1	44.8	11.0	4.1	18.3	23.0
ASB outlet pond 1	11.6	15.4	22.2	35.1	33.2
Mill P					
Primary clarifier inlet	39.9	34.1	16.1	13.4	43.0
Primary clarifier outlet	64.7	46.7	22.0	42.5	51.6
ASB inlet	81.4	46.0	59.1	57.7	44.0
ASB outlet	32.8	29.5	21.1	31.2	NA
Overall Range	3.1 - 81.4	8.7 - 46.7	3.9 - 59.1	9.3 - 61	17.7 - 88
Overall Average	38.9	29.8	20.6	34.2	41.0

NA = not applicable, concentration below lower calibration limit

5.0 SUMMARY AND CONCLUSIONS

This research indicates that NCASI Method RSC-02.02 is effective for assessing total sulfide, MeSH, DMS, DMDS, and DMTS in pulp and paper mill wastewaters. The method utilizes a separate preservation and injection for determinations of total sulfide and ORSCs. Samples are preserved with zinc acetate at pH 10 for total sulfide and with ascorbic acid at pH 2.5 for ORSCs. All samples are acidified (pH <2.5) prior to direct injection on the GC and are detected using a PFPD. The applicable method range is ~20 to 1000 μg S/L without sample dilution, and can be extended above that range using sample dilution prior to acidification and analysis.

Method validation results indicate good agreement between concentrations determined using a quadratic fit equation for over 17 calibration curves and gravimetrically determined concentrations of standards. Daily calibration verifications yielded average recoveries of 106% for total sulfide (n=94) and average recoveries of 95 to 102% for ORSCs (n=42). Method blanks were free of the target analytes (n=94). Precision and accuracy were assessed using surrogate spikes, matrix spikes, and replicate analyses. Surrogate recoveries for total sulfide, MeSH, DMS, DMDS, and DMTS in over 1077 pulp and paper mill wastewater samples ranged from 73 to 131%, with an average of 106%. Matrix spike recoveries averaged 93, 106, 102, 112, and 96% for total sulfide, MeSH, DMS, DMDS, and DMTS, respectively. Precision results as reflected by pooled RPDs for duplicate analyses ranged from 2.1 to 5.3% for all target analytes. Storage stability using method-specified preservations indicated stability of the samples for up to 14 days. Injection pH significantly impacted recovery of total sulfide, with pH 2.5 yielding the highest recovery (96%).

The method was effectively applied to a variety of samples collected throughout WWTPs and some process sewers from over 20 pulp and paper mills. Results were highly variable. Variability may have been due to changes in matrices over time or to sampling techniques. Throughout several studies to assess variability at selected sampling sites, RSDs were 38.9% for total sulfide, 29.8% for MeSH, 20.6% for DMS, 34.2% for DMDS, and 41.0% for DMTS. This is well above the variability of ~5% observed for the analytical method alone.

Results of investigations conducted in conjunction with odor reduction studies at 20 mills yielded a wide range of RSC concentrations from similar locations within WWTPs. These data are not necessarily reflective of industry-wide concentrations because the participating mills were in the process of investigating odor sources. Median concentrations at primary clarifier outlets were 3.5 mg S/L for total sulfide, 38 μg S/L for MeSH, 66 μg S/L for DMS, 22 μg S/L for DMDS, and <20 μg S/L for DMTS. Median concentrations at the fronts of ASBs were 2.9 mg S/L for total sulfide, 60 μg S/L for MeSH, 68 μg S/L for DMS, 68 μg S/L for DMDS, and <20 μg S/L for DMTS. Median concentrations from midpoints of ASBs were 0.29 mg S/L for total sulfide and <20 μg S/L for ORSCs. Final effluent sample medians were <20 μg S/L for all target analytes.

NCASI Method RSC-02.02 has proven to be an effective tool for investigating odorous compounds in pulp and paper mill wastewater treatment plants.

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APPENDIX A

NCASI METHOD RSC-02.02

REDUCED SULFUR COMPOUNDS BY DIRECT INJECTION GC/PFPD

1.0 SCOPE AND APPLICATION

1.1 This method is used for the determination of the reduced sulfur compounds (RSCs) total sulfide as hydrogen sulfide (H_2S) [7783-06-4], methyl mercaptan (MeSH) [74-93-1], dimethyl sulfide (DMS) [75-18-3], dimethyl disulfide (DMDS) [624-92-0], and dimethyl trisulfide (DMTS) [3658-80-8] in wastewaters from pulp and paper mills. The RSCs are measured by direct aqueous injection gas chromatography with pulsed flame photometric detection (GC/PFPD).

1.2 The concentration of sulfide (H_2S) measured using this method represents the total amount of sulfide in the sample volatile at pH 2.5. It is believed that this includes all freely dissolved sulfide plus sulfide weakly associated with either dissolved organic matter or certain transition metals. If native sample pH is greater than 2.5, the actual total sulfide concentration in solution might be less than the concentration measured by this method.

1.3 The method has been applied to influent to wastewater treatment, samples from within the wastewater treatment system, and effluent from wastewater treatment.

1.4 This method has been validated for a single laboratory.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of chromatograms. Each analyst must demonstrate an ability to generate acceptable results with this method.

2.0 SUMMARY OF THE METHOD

2.1 Samples are collected directly from the aqueous process stream or wastewater basin using appropriate collection vessels. Samples require two different preservation techniques to preserve all analytes. Samples are kept refrigerated until analysis.

2.2 In the laboratory, an aliquot of the sample is transferred to a 2-mL sealed vial. An aliquot of an internal standard solution is added to each of the vials. The sample is acidified (total sulfide only) and injected into the GC with a split injection. The GC column is temperature programmed to separate the analytes from other compounds which may be present in the sample. The analytes are selectively detected with a PFPD.

2.3 Identification of the RSCs is determined by comparison of their relative retention times with the relative retention times of an internal standard. If the results are questionable, confirmation using a second column may be necessary.

2.4 The RSCs are quantified by comparison with liquid standards using the internal standard technique. Multiple standards are analyzed to cover a calibration range of 20 to 1000 µg S/L. Calibration to lower concentrations may be possible for some compounds. Dilution is required to analyze samples with concentrations above 1000 µg S/L.

2.5 The method detection limit was calculated using the USEPA procedure in 40 CFR Part 136 Appendix B (Federal Register 1984) in a final effluent collected from an unbleached kraft mill after allowing the sulfide level to drop to less than 50 µg S/L. The method detection limit determined for total sulfide was 32.0 µg S/L. The sensitivity of the method has not been determined for MeSH, DMS, DMDS, and DMTS, and the detection limits have not been established. MeSH, DMS, DMDS, and DMTS have been successfully calibrated down to concentrations of 20 µg S/L.

2.6 Data quality is assured with ongoing recovery assessments, duplicate analyses, surrogate recovery experiments, matrix spike experiments, and blank analyses. MeSH, DMS, and DMDS standards are checked by comparing the results with an independently prepared standard. The sulfide standard is verified by independent analysis using EPA Methods 376.1 and 376.2.

3.0 DEFINITIONS

3.1 The definitions below are specific to this method, but conform to common usage as much as possible.

3.1.1 µg/L – micrograms of compound per liter

3.1.2 µg S/L – micrograms of sulfur per liter

3.1.3 May – this action, activity, or procedural step is neither required nor prohibited

3.1.4 Must not – this action, activity, or procedural step is prohibited

3.1.5 Must – this action, activity, or procedural step is required

3.1.6 Should – this action, activity, or procedural step is suggested, but not required

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, injection port liners, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analyses by running laboratory blanks.

4.2 Glassware must be scrupulously cleaned, and glassware that comes in contact with concentrations less than 50 µg S/L may need to be deactivated. Glassware can be deactivated either by soaking in acid followed by silylation or by Siltek™ coating as described in Section 6.1.1. After use, clean all glassware by washing with mild detergent in hot water and rinsing with tap water. The glassware should then be drained until completely dry.

4.3 It is required that all metal surfaces that come in contact with the sample be deactivated. This includes injection port liners, seals, and syringe needles. Deactivate the metal surfaces as described in Section 6.1.1.3.

4.4 The internal standard, thiophene, may be present in some pulp mill process streams. If the composition on a matrix is unknown, a sample analyzed without internal standard should be examined for the presence of thiophene. The surrogate, thioanisole, can be used as an internal standard if interference with thiophene is identified.

4.5 Some compounds can interfere with the chromatography if the separation is not efficient. Specific interference includes partial coelution of carbon disulfide with dimethyl disulfide. When performed properly, this method separates these compounds sufficiently. During the development of the method, carbon disulfide was not detected in any of the wastewater samples analyzed.

4.6 After a number of injections of samples, a sulfur dioxide artifact peak can interfere with methyl mercaptan. A clean, deactivated injection port liner should be installed after approximately 20 sample injections. The injection port gold seal should also be cleaned with deionized water, methanol, and acetone using a long cotton swab prior to inserting the clean injection port liner during liner changes.

5.0 SAFETY

5.1 All chemicals should be treated as potential health hazards. It is recommended that prudent practices for handling chemicals in the laboratory be employed (NRC 1995).

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.3 The RSCs are either flammable gases or liquids that may be harmful if inhaled or ingested. These compounds can also cause a considerable nuisance odor. Use them in a laboratory fume hood and wear appropriate gloves, eye protection, and other protective clothing.

6.0 EQUIPMENT AND SUPPLIES

Note: *Brand names and suppliers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and material other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Sampling Equipment

6.1.1 Samples are to be collected in amber glass bottles with minimal headspace. It is recommended that 40-mL amber, borosilicate glass vials with Teflon™ faced silicone backed lids (VOA vials) be used. Although passivation of glassware for RSC compounds is common practice, passivation of sample containers during this study has not been found to be necessary in the standard operating range of this method. Some improvement of the lower level calibration response has been found when using passivated autosampler vials. If passivation of glassware is desired, one of the following techniques can be used.

6.1.1.1 Soak clean glassware in a 10% HCl solution for at least one hour. Rinse the glassware thoroughly with water, followed by an acetone rinse, air drying, and treatment with 5% dimethyldichlorosilane in toluene. Rinse the glassware with toluene, methanol, and water, then air dry it.

6.1.1.2 Treat clear VOA vials with the Siltek deactivation process (Restek Corporation, Bellefonte, PA). Caution: strong caustic detergents will remove the Siltek coating.

6.1.1.3 Treat syringe needles by slowly pumping a 15% solution of BSTFA in hexane three times followed by a rinse with acetone, methanol, and water.

6.1.2 The use of automatic sample collection equipment has not been validated for this method and should not be incorporated until its effectiveness has been proven.

6.2 Laboratory Glassware and Supplies

6.2.1 Amber 2-mL autosampler vials deactivated if desired by one of the methods described in Section 6.1.1

6.2.2 Volumetric flasks (10-mL, 50-mL)

6.2.3 Syringes (including gas-tight syringes) deactivated by methods described in Section 6.1.1.3

6.3 Analytical Equipment

6.3.1 Gas chromatography system – gas chromatography analytical system complete with a cryogenically cooled, temperature programmable gas chromatograph with a split/splitless injection port and all required accessories including syringes, analytical columns, and gases

6.3.2 Injection port liner – 4-mm deactivated (silanized or Siltek) straight glass liner lightly packed with a plug of deactivated (silanized) quartz two-thirds the distance from the septum end of the liner (Section 17, Figure 1)

6.3.3 Column – 30 m x 0.25 mm x 1.4 μm, 6% cyanopropylphenyl 94% dimethylpolysiloxane bonded phase (624 phase) fused silica capillary column

6.3.4 GC detector – pulsed flame photometric detector (OI Analytical or equivalent) with appropriate data system

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Deionized (DI) water should be tested immediately before use to verify the absence of any target analytes. If the water is contaminated, it may be necessary to prepare fresh deionized water, purge the water with nitrogen or helium, or boil the water to remove the contaminant(s).

7.1.2 Prepare phosphoric acid solution by combining one part of phosphoric acid (reagent grade) with three parts deionized water.

7.1.3 Prepare acidified DI water by adding phosphoric acid solution (Section 7.1.2) to DI water (Section 7.1.1) until the pH is between 2.3 and 2.7. It takes approximately 0.5 mL of acid in 1 L of water to reach this pH.

7.1.4 L-Ascorbic acid (ACS reagent grade)

7.1.5 Methanol (distilled in glass)

7.1.6 Prepare the zinc acetate solution (40 mmole/L) by adding 1.75 g of zinc acetate dehydrate (reagent grade) to 200 mL of DI water. Slowly adjust the pH drop wise by adding 1N NaOH while stirring the DI water containing the zinc acetate (this takes 20 to 30 minutes). Dropwise addition is important up to pH 8.0 in order to produce small crystals of the resulting salt which will homogenize upon shaking. Once pH 8.0 is achieved dropwise addition is not longer required. Finish adjusting the pH to between 12 and 12.5 using the 1N NaOH solution (total 1N NaOH required is approximately 20 mL). This solution should produce a fine, even suspension which does not settle rapidly. If you shake the container and then let it sit, it will usually remain in suspension for over 20 minutes.

7.1.7 Prepare dimethyldichlorosilane (DMDCS) 5% in toluene by adding 25 mL of DMDCS to 475 mL of toluene. It is also available as a mixture from Supelco as Sylon CT.

7.1.8 Prepare N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) 15% in hexane by adding 1.5 mL of BSTFA to 8.5 mL of hexane.

7.1.9 Toluene (distilled in glass)

7.1.10 Hexane (distilled in glass)

7.1.11 $CaCl_2$ desiccant, 96%+ ACS reagent grade

7.1.12 Prepare NaOH 1 N by dissolving 40 g of pellets (97+%) into 1 L of DI water.

7.2 Analytical Standards

Analytical standards are prepared from pure standards. Reported purity should be greater than 95% for all the neat material used.

7.2.1 Prepare the internal standard primary solution by weighing 26 mg (to the nearest 0.1 mg) of thiophene and diluting to 10 mL in volumetric flasks with methanol. Prepare the primary standard at a concentration of approximately 1 mg S/mL. Calculate the actual concentration using Equation 1.

Equation 1

$$C_S = \frac{(m * FS)}{V_S}$$

where: C_S *is the concentration of sulfur in the standard (mg S/mL)*
m *is the mass of the compound added to the standard (mg)*
FS *is the fraction of sulfur in the compound (Section 17, Table 6 except for* $NaS_2 \bullet 9H_2O$*, which is 0.1335)*
V_S *is the total volume of the standard (mL)*

7.2.2 Prepare the surrogate standard primary solution by weighing, to the nearest 0.1 mg, 40 mg of thioanisole and diluting to 10 mL in volumetric flasks with methanol. Prepare the primary standard at a concentration of approximately 1 mg S/mL. Calculate the actual concentration using Equation 1.

7.2.3 Prepare a combined internal standard and surrogate working solution by adding 400 µL of each primary stock (Sections 7.2.1 and 7.2.2) to a 10-mL volumetric flask and

diluting to the mark with methanol. The concentration in the solution is approximately 40 µg S/mL for each compound.

7.2.4 Prepare a primary and working standard of sulfide from sodium sulfide nonahydrate (Na_2S). The $Na_2S \bullet 9H_2O$ should be either opaque or white crystals. This material is hydroscopic and will turn into a slurry if not stored in a dry environment such as a desiccator containing anhydrous $CaCl_2$ and wrapped with tape to seal the bottle. It will also turn yellow or green (elemental sulfur) in storage. Prepare the working solution by adding 340 mg of zinc acetate dihydrate to 40 mL of purged DI water. Slowly adjust the pH drop wise by adding 1N NaOH while stirring the water containing the zinc acetate (this takes 10 to 20 minutes). Dropwise addition is important up to pH 8.0 in order to produce small crystals of the resulting salt which will homogenize upon shaking. Once pH 8.0 is achieved dropwise addition is not longer required. Finish adjusting to between 10.5 and 11 using the 1 N NaOH solution. Add 38 mg of $Na_2S \bullet 9H_2O$, weighed to the nearest 0.1 mg, while continuing to stir for 5 minutes. his solution should be a well dispersed suspension with no visible clumping of the solids. Transfer the solution quantitatively into a 50-mL volumetric flask and dilute to the mark with purged DI water. The concentration in the solution will be approximately 100 µg S/mL, with an equivalent total sulfide concentration of 106 µg/mL. Calculate the actual concentration using Equation 1. The fraction of sulfur (FS) in $Na_2S \bullet 9H_2O$ is 0.1335.

7.2.5 Prepare a primary solution of MeSH by slowly bubbling MeSH gas into a tared 10-mL volumetric flask containing methanol. Allow the MeSH to dissolve into the methanol until approximately 15 mg (weighed to the nearest 0.1 mg) has been added. This corresponds to approximately 7.5 mL of pure gas at room temperature. Use a thin (1/16 inch) Teflon line to transfer the MeSH into the methanol and be sure that any methanol clinging to the line is knocked back into the volumetric flask before measuring the final weight. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.6 mg/mL as MeSH. Calculate the actual concentration using Equation 1.

7.2.6 Prepare a primary solution of DMS by weighing 19 mg (to the nearest 0.1 mg) of DMS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.9 mg/mL as DMS. Calculate the actual concentration using Equation 1.

7.2.7 Prepare a primary solution of DMDS by weighing 15 mg (to the nearest 0.1 mg) of DMDS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.5 mg/mL as DMDS. Calculate the actual concentration using Equation 1.

7.2.8 Prepare a primary solution of DMTS by weighing 13 mg (to the nearest 0.1 mg) of DMTS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.3 mg/mL as DMTS. Calculate the actual concentration using Equation 1.

7.2.9 Prepare a working solution of MeSH by adding 1.0 mL of the primary solution (Section 7.2.4) to a 10-mL volumetric flask and diluting with methanol. MeSH is not stable when mixed with the other standards.

7.2.10 Prepare a primary solution of carbon disulfide (CS_2) by weighing 12 mg (to the nearest 0.1 mg) of CS_2 into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.2 mg/mL as CS_2. Calculate the actual concentration using Equation 1.

7.2.11 Prepare a working solution of mixed RSCs and CS_2 by adding 1.0 mL of the primary solutions of DMS (Section 7.2.6), DMDS (Section 7.2.7), DMTS (Section 7.2.8), and CS_2 (Section 7.2.10) to a 10-mL volumetric flask and diluting with methanol.

7.3 Calibration Standards

7.3.1 Prepare a multilevel calibration working solution by adding 500 µL of each of the individual working solutions of sulfide (Section 7.2.4), MeSH (Section 7.2.9), and mixed RSCs (Section 7.2.11) to a 5-mL volumetric flask. Dilute to the mark with purged DI water and adjust the pH to around 2.5 with phosphoric acid solution. The calibration working solution has limited stability and should be prepared the day it is used.

7.3.2 Prepare a nominal 20 µg S/L calibration standard by adding 4.0 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosample vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

Equation 2

$$C_{cal} = \frac{C_{WS} * V_{WS}}{V_{cal}}$$

where: C_{cal} *is the concentration of the analyte/internal standard in the calibration standard (µg S/L)*
C_{WS} *is the concentration of the analyte in the working solution (µg S/mL)*
V_{WS} *is the volume of working solution added to the calibration standard (mL)*
V_{cal} *is the volume of the calibration standard (0.002 L)*

7.3.3 Prepare a nominal 50 µg S/L calibration standard by adding 10 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.4 Prepare a nominal 200 µg S/L calibration standard by adding 40 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.5 Prepare a nominal 500 µg S/L calibration standard by adding 100 µL of the multipoint calibration solution (Section 7.3.1) to 1.7 mL of pH 2.5 adjusted DI water in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.6 Prepare a nominal 1000 µg S/L calibration standard by adding 200 µL of the multipoint calibration solution (Section 7.3.1) to 1.6 mL of pH 2.5 adjusted DI water in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.1) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.7 Prepare a daily calibration check standard (200 µg S/L) by adding 4.0 µL of the working standards of sulfide (Section 7.2.4), MeSH (Section 7.2.9), and mixed RSCs (Section 7.2.11) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.1) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.8 When preparing standards or samples, the autosampler vial has an air bubble after being sealed. This is important so that the analyte and internal standard spikes can be mixed well before analyzing the sample or standard. At least three good inverted shakes should be performed before injecting the standard or sample.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collection

Collect grab samples directly from the process liquid stream using appropriate collection vessels, typically 40-mL VOA amber vials. Fill each vial with the sample, leaving minimum headspace. Collect a separate sample for analyzing total sulfide because of the preservation technique. A substantial quantity of preservative is required, so a dilution factor is needed to correct for dilution due to preservation. This can be accomplished by measuring the volume of preservative added and the final volume of the sample including preservative.

8.2 Preservation

8.2.1 Preservation for the analysis of MeSH, DMS, DMDS, and DMTS requires the addition of 120 mg of ascorbic acid to a 40-mL VOA vial (3 g/L) and pH adjustment to <2.5 with phosphoric acid solution. To adjust the pH, add a representative sample to an extra vial containing ascorbic acid. Measure the volume of phosphoric acid required to reach the target pH and discard that sample. Use that volume of acid to adjust the samples to be analyzed. If the volume of acid needed is less than 2 mL, no correction for dilution is required.

8.2.2 Preservation for the analysis of total sulfide requires the addition of 5 mL of zinc acetate solution (Section 7.1.6) to a 40-mL VOA vial. The final pH of the sample should be greater than 10. Adjust the pH with 1 N NaOH solution if necessary. A correction for the dilution of the sample by the preservative must be made. For example, if 35 mL of sample is diluted to 40 mL, the measured concentration should be multiplied by a dilution factor of 1.14. Sample volumes can be measured gravimetrically or using calibrated glassware (graduated cylinder).

8.3 Storage

All samples must be stored in a refrigerator (4°C) until analysis. Storage stability has been found to be matrix-dependent. Using the prescribed preservation techniques, greater than 80% recovery was found for all compounds in both a bleached kraft mill effluent and an unbleached kraft mill effluent after 14 days of storage. Storage of zinc acetate preserved samples with native concentrations of <0.1 mg S/L collected in highly aerated portions of WWTP have yielded increasing concentrations of total sulfide over time.

9.0 QUALITY CONTROL

To control the quality of the data generated using this method, an initial calibration check, independent standard check, daily blank checks, daily calibration checks, surrogate recovery experiments, periodic duplicates, and periodic matrix spikes should be performed.

9.1 Initial Calibration Check

A multipoint internal standard calibration should be performed covering the operating range of the method (20 to 1000 µg S/L). A wider or narrower range is acceptable if all sample concentrations fall within that range. The criterion for acceptable linearity is a mean absolute percent error (MAPE) for the curve of less than or equal to 20% (Section 10.2.3).

9.2 Independent Standard Check

When a primary standard is prepared for calibration and matrix spike experiments, it should be compared with an independent standard either prepared from another source of compound or obtained from a certified standard vendor. Only methyl mercaptan, dimethyl sulfide, and dimethyl disulfide are commercially available as solutions in methanol at this time (Crescent Chemicals). The independent standard should match the primary standard used for calibration and matrix spikes within 30%. This check will minimize bias due to errors in standard preparation.

9.3 Daily Blank Checks

A daily blank check should be performed before running samples. A blank check should be performed if carryover is suspected (e.g., after running a sample outside the calibration range). A blank check consists of analyzing 1.8 mL of purged DI water with internal standard and surrogate as described in Section 11.1. The RSC level in the blank should not exceed 20% of the lowest calibration point (4 µg S/L for MeSH, DMS, DMDS, and DMTS; 6 µg S/L for total sulfide).

9.4 Daily Calibration Checks

Prepare and analyze a mid-level calibration point every day that samples are analyzed. The percent recovery of each compound in the standard should be within 20% of the percent recovery of the same calibration level in the multipoint calibration. If the daily calibration check fails, it should be repeated. If it fails a second time, the standards (working, primary, internal standard) should be re-prepared. If it continues to fail, the multipoint calibration should be repeated. A summary of single laboratory daily calibration checks for this method is provided in Section 17, Table 1.

9.5 Surrogate Recovery Check

In this method thioanisole is utilized as a surrogate for the reduced sulfur compounds. All samples are spiked with 9 μL of the thioanisole spiking solution (Section 7.2.1) to monitor surrogate recovery. The percent recovery of the surrogate should be determined and the results charted to document the surrogate recovery of the method. Performance criteria for acceptable surrogate recovery, as determined during a single-laboratory validation of this method, are presented in Section 17, Table 2.

9.6 Duplicate Analyses

A duplicate sample should be analyzed with each set of samples (batch of samples no greater than 20). Duplicate analysis requires the analyses of separate aliquots of the sample. The relative percent difference between the two samples should be calculated and charted to estimate the method's precision. Section 17, Table 3 lists the relative percent differences found during a single laboratory validation of the method.

9.7 Matrix Spike Analyses

A matrix spike analysis should be performed with each set of samples (batch of samples no greater than 20). A known amount of the RSC working solutions should be added to a sample so that the native plus the spike level of each RSC is at least one times the native level. The percent recovery of the matrix spike should be determined and the results charted to document the recovery of the method. Section 17, Table 3 lists the recovery found during single laboratory validation studies.

9.8 Field Replicates and Field Spikes

Depending on specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of sampling and sample transporting techniques.

9.9 Resolution Checks

The resolution of the separation should be checked periodically (ideally on a daily basis) by measuring the valley between the DMS and CS_2 peaks. The valley should be less than 10% of the average peak heights of the two peaks. If the valley is 10% or greater, maintenance of the injection port and/or column is necessary.

10.0 CALIBRATION AND STANDARDIZATION

10.1 GC/PFPD Operating Conditions

Assemble the GC/PFPD and establish the operating conditions outlined in Section 17, Table 4. Use the conditions specified by the PFPD manufacturer to optimize for the detection of sulfur compounds. Once the GC/PFPD system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration checks, and quality assurance samples.

If excessive peak broadening is observed for sulfide and MeSH, a pressure pulse during the injection might keep the injection focused on the column. This has been necessary when using autoinjectors with a rapid injection stroke. An initial pressure of 30 psi for 0.2 min followed by a rapid drop back to a constant flow of 1.2 mL/min sharpened the early eluting peaks. Keep the pressure pulse time to a minimum because the PFPD loses its sulfur response at high carrier gas flow rates.

10.2 Initial Multipoint Calibration

The square root of the PFPD response for sulfur is approximately linear with respect to concentration over the operating range of the method. To demonstrate this and establish a calibration function for the method, prepare and analyze calibration standards to cover this range. The internal standard calibration approach should be used for this method. Calibrate the RSCs using concentrations normalized to the sulfur content of the standard. The use of sulfur concentrations ensures that the concentrations prepared cover the operating range of the detector. It also allows the relative response factors to be checked, because, theoretically, they should all be 1.

10.2.1 Determine the retention times of the analytes by analyzing a daily calibration solution (Section 7.3.7). A chromatogram similar to that shown in Section 17, Figure 2 should be obtained. Identify the peaks and determine their relative retention times using Equation 3. Section 17, Table 6 lists the relative retention times for the RSCs using this method.

Equation 3

$$RRT_i = \frac{RT_i}{RT_{IS}}$$

where: RRT_i *is the relative retention time for compound i*
RT_i *is the retention time for compound i*
RT_{IS} *is the retention time for the internal standard*

10.2.2 Prepare a five-point calibration curve to determine the relationship between instrument response and concentration over the operating range for each analyte. Analyze each of the calibration standards prepared as described in Sections 7.3.2 through 7.3.7.

10.2.3 The results of the calibration standard analyses for each compound are either fitted to a quadratic equation or described by an average relative response factor using internal standard calibration techniques. To find the best quadratic fit for the data, plot the response ratio of each compound as calculated in Equation 4 versus the ratio of the standard concentration versus the internal standard concentration. Curve-fitting software either in the data system (e.g., Agilent Chemstation) or external to the data system (e.g., Excel) can be used to fit the best quadratic equation in the form of Equation 5.

Equation 4

$$RR = \frac{A_i}{A_{IS}}$$

where: RR is the response ratio
A_i is the area of the peak for compound i
A_{IS} is the area of the internal standard peak

Equation 5

$$RR_i = a + b * C_R + c * C_R^2$$

where: RR is the response ratio
a is the y-intercept from the quadratic regression
b is the linear constant from the quadratic regression
C_R is the ratio of the compound concentration versus the internal standard concentration
c is the quadratic constant from the quadratic regression

If the calibration criteria cannot be met using a quadratic fit, the average response factor can be used. Calculate the average response factor by finding the mean of the relative response factors calculated for each concentration of standard, as shown in Equation 6.

Equation 6

$$RRF_i = \left(\frac{A_i \times C_{IS}}{A_{IS} \times C_{cal}} \right)$$

where: RRF_i is the relative response factor for compound i
A_i is the area of the peak for compound i
A_{IS} is the area of the internal standard peak
C_{cal} is the concentration as sulfur in the calibration standard (µg S/L)
C_{IS} is the concentration of internal standard as sulfur (µg S/L)

To evaluate the closeness of the fit for the calibration, use the calibration model chosen (quadratic curve or average response factor) to calculate the concentration for each calibration level. Use Equation 7 to calculate the concentration using the quadratic model or Equation 8 to calculate the average response factor model. Determine the error for each level and calculate the mean absolute percent error (MAPE) as shown in Equation 9. The MAPE is used by software packages such as SAS and Statgraphics to evaluate the fit between a model prediction and the measured values.

Equation 7

$$C_i = \frac{\left(-b + \sqrt{b^2 - 4c(a - RR)}\right)}{2c} * C_{IS}$$

where: C_i *is the measured concentration of compound i (µg S/L)*
a is the y-intercept from the quadratic regression
b is the linear constant from the quadratic regression
c is the quadratic constant from the quadratic regression
RR is the response ratio
C_{IS} *is the concentration of internal standard as sulfur (µg S/L)*

Equation 8

$$C_i = \frac{RR}{RRF} * C_{IS}$$

where: C_i *is the measured concentration of compound i (µg S/L)*
RR is the response ratio
RRF is the relative response factor
C_{IS} *is the concentration of internal standard as sulfur (µg S/L)*

Equation 9

$$MAPE = \frac{\sum \left| \frac{C_{cal} - C}{C_{cal}} \right| * 100}{n}$$

where: MAPE is the mean absolute percent error
C_{cal} *is the concentration in the calibration standard*
C is the concentration measured for the calibration level
n is the number of calibration levels

The MAPE should be below 20% for each compound. Section 17, Table 5 lists the MAPE found for several calibrations using both an average and a quadratic calibration model. Section 17, Figure 3 shows a typical calibration curve for the PFPD response with a quadratic fit.

If a 20% MAPE cannot be achieved, one or more of the following actions should be taken.

10.2.3.1 Standards should be reanalyzed if the analysis appears to be suspect due to large variation from predicted response.

10.2.3.2 Standards should be reprepared if they appear to be suspect after reanalysis.

10.2.3.3 System maintenance should be performed, including replacing the injection port liner, replacing the septum, clipping the column, checking the split ratio, and checking the detector parameters.

10.2.3.4 The calibration range may be reduced by eliminating the low level or high level calibration standard. If the calibration range is changed, do not report values that are measured outside this range. This is especially true for the quadratic model, where large errors can occur.

10.3 Daily Calibration Check

Prior to analyzing samples each day, a daily calibration check should be prepared (Section 7.3.7) and analyzed. Calculate the percent recovery of the standard using Equation 10 to verify the calibration. In-house percent recovery control limits should be determined, and should not exceed ±20%. If the calibration check does not pass, the action items in Section 10.2.3 should be repeated. If these fail, the initial multipoint calibration should be repeated. Section 17, Table 1 summarizes the results for daily calibration checks during the method evaluation and subsequent single laboratory analyses.

Equation 10

$$R = \left(\frac{C_i}{C_{IC}} \right) \times 100$$

where: R is the recovery in percent
C_i is the measured concentration for compound i (µg S/L)
C_{IC} is the concentration measured during the initial calibration (µg S/L)

10.4 BLANK ANALYSIS

A method blank should be prepared and analyzed with the initial calibration and every day on which samples are analyzed. Prepare the blank the same as the calibration standards, but only add the internal standard solution (Section 7.3). The blank concentration should be less than 20% of the lowest calibration point. High blank levels can be caused by contaminated reagent water/acid, contaminated internal standard, contaminated glassware or syringes, and dirty injection ports. Resolution of sulfur dioxide, a common contaminate, from methyl mercaptan is critical for meeting the blank criteria. Section 17, Figure 4 shows a typical sample with MeSH resolved from the artifact peak.

11.0 PROCEDURE

11.1 Sample Analysis

Transfer a known volume (1.8 mL) of the sample to an autosampler vial using a deactivated gas-tight syringe. If the sample is preserved at pH 2.5, no pH adjustment is required. If the sample is preserved at pH 10, phosphoric acid solution should be added to bring the pH to between 1.5 and 2.5. Determine the amount of acid needed using a trial sample, then add the determined amount to the sample to be analyzed (typically 15 to 20 µL). Add 9 µL (assuming a sample volume of 1.8 mL) of the internal standard solution (40 mg S/L thiophene and thioanisole) to the vial. Be sure that the spike goes into the sample liquid and that it is well mixed (Section 7.3.8). Inject the sample using the exact instrumental conditions used for the

analysis of the calibration standards (Section 10.1). Calculate the concentration of each RSC using Equation 7 or 8, depending on the calibration model. If the concentration is above the calibration range, the sample must be diluted and reanalyzed.

11.2 Dilution

If dilution is necessary, inject some fractional volume less than 1.8 mL into the vial using a deactivated gas-tight syringe, bring it to 1.8 mL with DI water pH adjusted to 2.5, and analyze it as described in Section 11.1. Calculate the dilution factor by dividing 1.8 mL by the volume of sample used. For samples preserved for total sulfide analysis, dilution by the preservative must also be accounted for by multiplying the two dilution factors together.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identification of Compounds

An analyte is identified by comparison of the relative retention time of the sample with the relative retention time of an authentic standard of the target compound analyzed using the same analytical conditions. Section 17, Table 6 lists the relative retention time windows for the RSCs and the absolute retention time windows for the internal standards.

12.2 Quantification of Compounds

Measure the concentration of each analyte as sulfur using Equation 7 or 8, then adjust for dilution and percent sulfur using Equation 11 to report the concentration as mass of compound instead of sulfur. The fraction of sulfur in each compound can be found in Section 17, Table 6.

Equation 11

$$C = \frac{C_i * DF}{FS}$$

where: C is the concentration of compound in the sample (µg/L)
C_i is the measured concentration for compound i (µg S/L)
DF is the dilution factor
FS is the fraction of sulfur in the compound

12.3 Duplicate Precision Estimate

Duplicate samples should be analyzed with each set of samples. Calculate the relative percent difference (RPD) for each duplicate pair as shown in Equation 12.

Equation 12

$$RPD = \frac{2 * |C_1 - C_2|}{(C_1 + C_2)} \times 100$$

where: RPD is the relative percent difference in the two determinations
C_1 is the first concentration measured (µg/L)
C_2 is the second concentration measured (µg/L)

12.4 MATRIX SPIKE CALCULATION

A matrix spike experiment should be performed with each set of samples analyzed. Calculate the percent recovery using Equation 13.

Equation 13

$$R = \frac{(C_{MS} - C)}{C_S} \times 100$$

where: R is the percent recovery
C_{MS} is the concentration measured in the matrix spiked sample (µg/L)
C is the concentration measured in the unspiked sample (µg/L)
C_S is the theoretical concentration of the spiked compound (µg/L)

13.0 METHOD PERFORMANCE

13.1 Single laboratory performance of this method is detailed in Section 17, Tables 2 and 3. Single laboratory precision is estimated to be 12.3% MeSH and 10% or less for the other RSCs. The average matrix spike recoveries ranged from 93 to 112% for all target analytes. The average surrogate spike recovery was 106%.

13.2 Interlaboratory precision estimates have not been determined for this method.

14.0 POLLUTION PREVENTION

14.1 The laboratory should check state and local requirements to determine if pollution prevention equipment is required or recommended in its area.

15.0 WASTE MANAGEMENT

15.1 It is the responsibility of the laboratory to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and lands by minimizing releases into the environment. Compliance with all sewage discharge permits and regulations is also required.

16.0 REFERENCES

16.1 Federal Register. 1984. Appendix B to Part 136–Definition and procedure for the determination of the method detection limit, rev. 1.11. *Federal Register* 49(209): October 26.

16.22 National Research Council (NRC) 1995. *Prudent practices in the laboratory*. Washington, DC: National Academy Press.

16.3 Taylor, J.K. 1987. *Quality assurance of chemical measurements.* Chelsea, MI: Lewis Publishers.

17.0 TABLES AND DIAGRAMS

Table 1. Results of Daily Calibration Checks

Compound	Mean Recovery	RSD (%)	n
Total sulfide	106	11.2	94
Methyl mercaptan	95.0	10.6	42
Dimethyl sulfide	100	10.5	42
Dimethyl disulfide	111	8.3	42
Dimethyl trisulfide	102	11.5	42

Table 2. Surrogate Recovery

Compound	Mean Recovery	RSD (%)	n
Thioanisole	106	6.7	1077

Table 3. Duplicate Results and Matrix Spike Recovery

	Duplicate Precision		Matrix Spike Recovery		
Compound	Pooled RSD[a] (%)	n	Mean Recovery (%)	RSD (%)	n
Total sulfide	9.4	87	93	20.7	70
Methyl mercaptan	12.3	33	106	20.0	33
Dimethyl sulfide	5.6	34	102	11.7	34
Dimethyl disulfide	7.0	33	112	16.5	34
Dimethyl trisulfide	4.7	25	96	24.1	34

[a] equation for pooled relative standard deviation can be found in Taylor 1987

Table 4. GC/PFPD Operating Conditions for Measuring Reduced Sulfur Compounds

Injection port	split (15:1 ratio)
Injection volume	2 µL
Split vent flow rate	16 mL/min helium
Injector temperature	110°C
Injection liner	4 mm id with fused silica wool packing (deactivated, either Siltek or Silanized)
Carrier gas	helium
Carrier gas flow rate	constant flow mode at 1.2 mL/min (pressure pulse at injection might be necessary see Section 10.1)
Column	J&W DB-624, 30 m x 0.25 mm id with 1.4 µm film fused silica capillary column or equivalent
Oven temperature program	
Initial	10°C
Ramp 1	6°C/min to 35°C for 2 minutes
Ramp 2	8°C/min to 170°C
Ramp 3	40°C/min to 250°C for 3 minutes
Detector	PFPD (OI model 5380 or equivalent)
Temperature	250°C
Combustion tube	2 mm
Optical filter	BG-12 (purple)
Hydrogen flow	11 mL/min
Air flows	optimized as described by manufacturer
Pulse rate	3.1 Hz
Signal	square root of PMT signal

Table 5. Summary of Initial Calibration Results

	Average Response Factor		Quadratic Fit			
Compound	Mean RRF[a]	Mean MAPE[b]	Mean a[c]	Mean b[d]	Mean c[e]	Mean MAPE[b]
Total sulfide	0.641	30.2	-0.073	0.838	-0.006	20.7
Methyl mercaptan	0.673	21.5	-0.074	0.906	-0.025	14.8
Dimethyl sulfide	0.887	18.0	-0.062	1.094	-0.013	14.8
Dimethyl disulfide	0.983	16.8	-0.092	1.385	-0.083	13.0
Dimethyl trisulfide	0.989	16.3	-0.092	1.401	-0.089	12.1

[a] average of eight calibration sets' mean relative response factors
[b] average of fifteen calibration sets' mean absolute percent errors
[c] average of eight calibration sets' y-intercepts from a quadratic regression
[d] average of eight calibration sets' linear constants from a quadratic regression
[e] average of eight calibration sets' quadratic constants from a quadratic regression

Table 6. Retention Time Statistics for RSCs and Sulfur Fraction

Compound	Mean[a] RRT	RSD[b] (%)	Relative Retention Time Window[c]	Fraction Sulfur
Total sulfide	0.192	1.12	0.186 – 0.198	0.9408
Methyl mercaptan	0.318	0.84	0.310 – 0.326	0.6665
Dimethyl sulfide	0.527	0.57	0.518 – 0.536	0.5160
Dimethyl disulfide	1.217	0.11	1.213 – 1.221	0.6808
Dimethyl trisulfide	1.748	0.19	1.738 – 1.758	0.7618
Internal standards	Mean RT[d] (min)	RSD[b] (%)	Retention Time Window	Fraction Sulfur
Thiophene	11.37	0.37	11.24 – 11.49	0.3810
Thioanisole	22.41	0.17	22.52 – 22.29	0.2581

[a] mean relative retention time (relative to thiophene) for 30 calibration standard analyses
[b] relative standard deviation for 30 calibration standard analyses
[c] windows are calculate from the mean value ± three times the standard deviation
[d] mean retention time for 30 calibration standard analyses

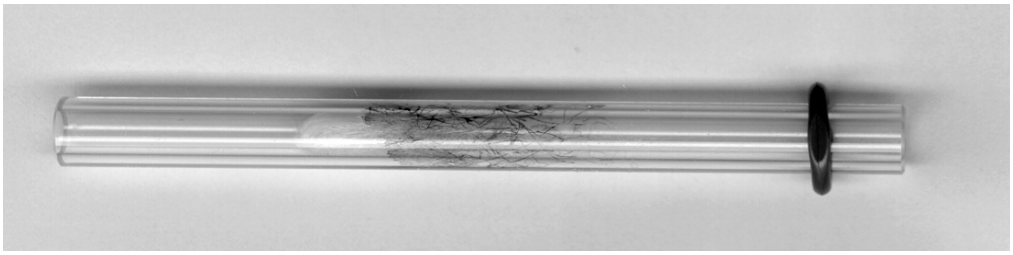

Figure 1. Injection Port Liner with Glass Wool Plug and Deposits from Approximately 20 injections Containing 3 g/L Ascorbic Acid

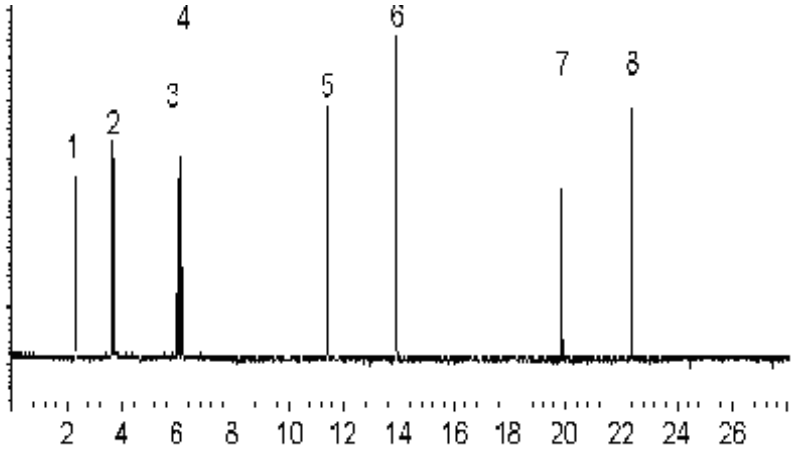

Figure 2. Chromatogram of 200 µg S/L Standard Containing (1) Total Sulfide; (2) MeSH; (3) DMS; (4) CS_2 (resolution check compound); (5) Thiophene (internal standard); (6) DMDS; (7) DMTS; (8) Thioanisole (internal standard)

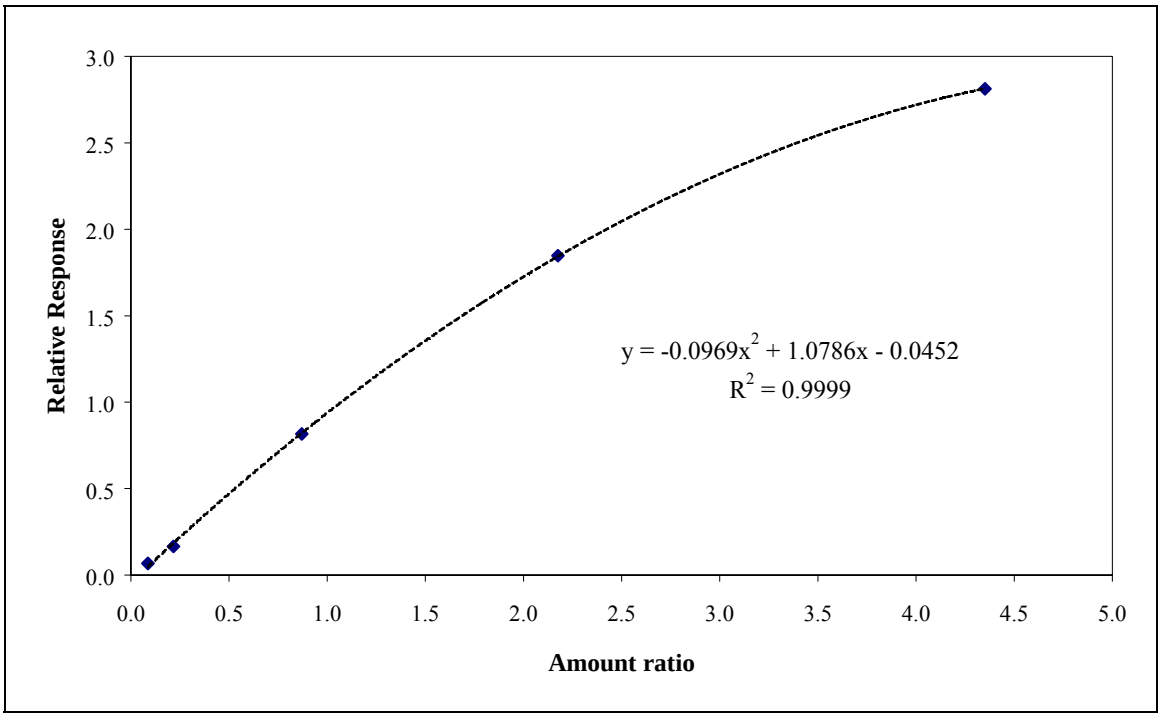

Figure 3. Typical Calibration Curve for Total Sulfide with Quadratic Equation

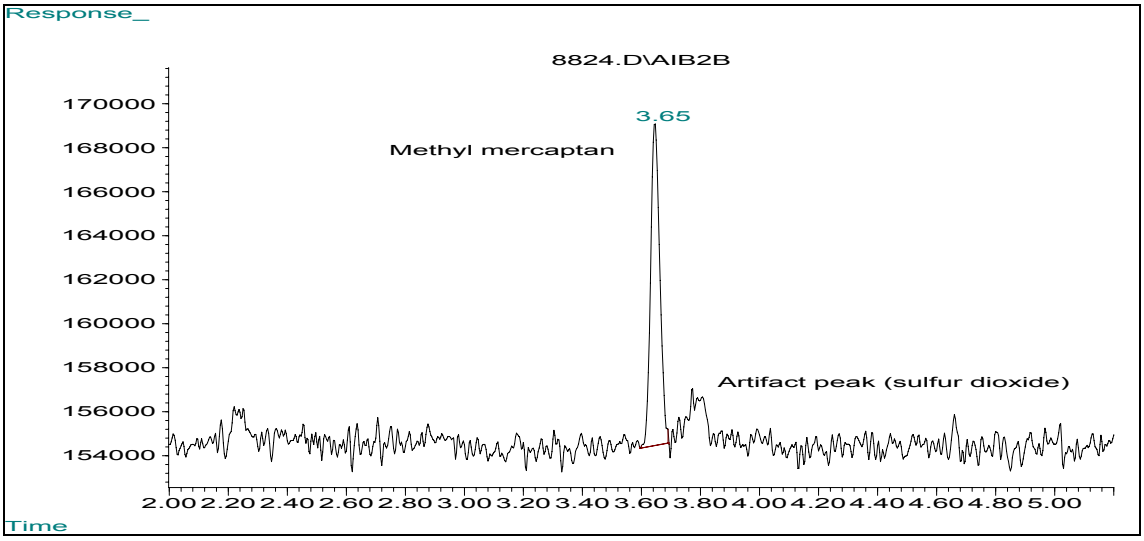

Figure 4. Separation of Methyl Mercaptan (100 µg S/L) from Artifact Peak in Pulp Mill Effluent

APPENDIX B

MILL SUMMARY DATA

MILL A

Mill A's production is nearly 520 metric tons per day (TPD) of bleached kraft pulp made predominately from softwood, Douglas-fir sawdust, and chips. A schematic of the wastewater treatment plant (WWTP) is provided in Figure B1. This mill hard pipes condensates to the WWTP just prior to the first ASB. Average daily water usage is 11 million gallons per day (MGD). Samples were collected from the primary clarifier outlet, front of the aerated stabilization basin (ASB), midpoint of the ASB, and final effluent. Results are provided in Table B1. Average biological oxygen demand (BOD_5) in the final effluent was 13 mg/L, average pH was 7.41, and total dissolved solids (TSS) were 23 mg/L.

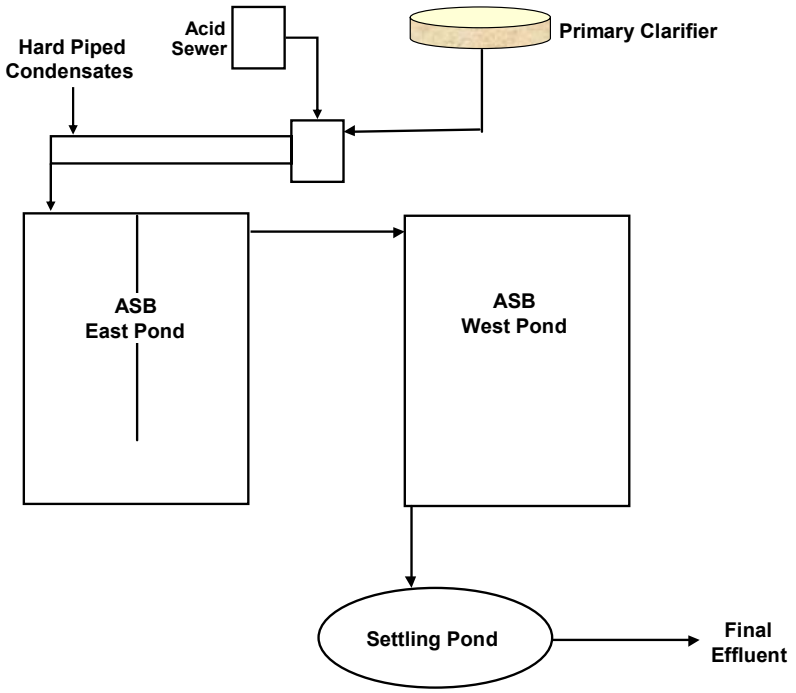

Figure B1. Mill A Wastewater Treatment Plant Schematic

Table B1. Mill A Reduced Sulfur Compound Concentrations (µg S/L)

Compound	Primary Clarifier Outlet	Front of ASB	Midpoint of ASB	Final Effluent
Total sulfide	18100	1030	530	225
MeSH	ND	39.4	232	56.9
DMS	ND	944	2260	33.5
DMDS	ND	1290	2550	113
DMTS	ND	25	353	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL B

This mill produces groundwood (GW), thermomechanical (TMP), and deinked pulp. Average daily production for GW is 8 air dried tons (ADT) of unbleached softwood pulp, TMP production averages 460 ADT, and the deinking facility's average daily production is 600 ADT. Average daily water usage is 11.5 MGD. The WWTP (Figure B2) consists of a 160 ft diameter primary clarifier, followed by a 90 MG ASB, an activated sludge (AS) plant consisting of a 4 MG aeration basin with a secondary clarifier, and a 50 MG ASB prior to discharge. The two ASBs have a total of 2175 horse power (HP) provided by 29 aerators. The retention time (RT) of the treatment system is 3 days. Secondary solids are removed from the secondary clarifier and split to the aeration basin as recirculated activated solids and to the primary clarifier as wasted activated solids. Solids removed from the treatment plant by the primary clarifier are dewatered and burned as fuel. Samples were collected from the primary clarifier outlet, ASB north lagoon, secondary clarifier, dewatering effluent, and final effluent. RSC results are listed in Table B2.

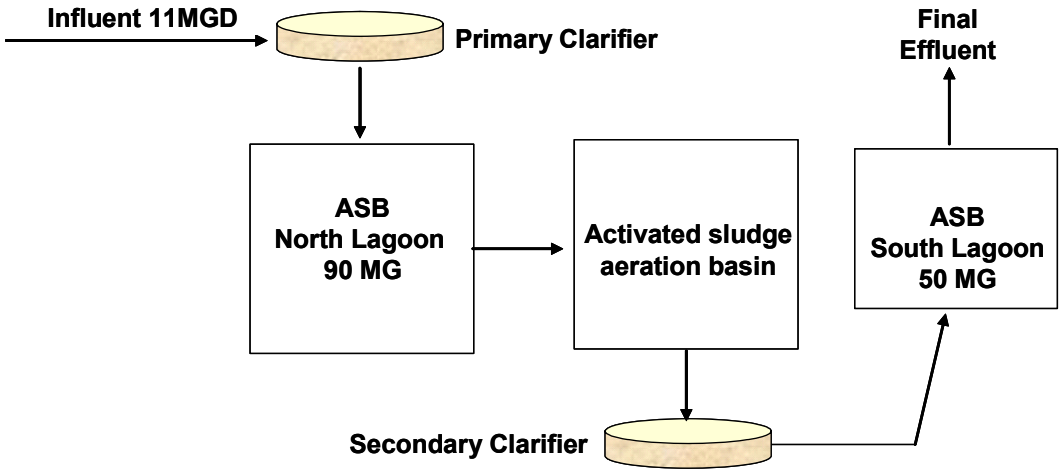

Figure B2. Mill B Wastewater Treatment Plant Schematic

Table B2. Mill B Reduced Sulfur Compound Concentrations (µg S/L)

Compound	Primary Clarifier Outlet	ASB North Lagoon	Secondary Clarifier	Dewatering Effluent	Final Effluent
Total sulfide	5320	52	48	609	ND
MeSH	190	ND	ND	83.3	ND
DMS	ND	ND	ND	ND	ND
DMDS	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL C

Mill C is a kraft mill pulping softwood and old cardboard containers (OCC). It produces about 550 tons of unbleached softwood pulp per day. Average water usage is 12 MGD. The mill is equipped with a primary clarifier, an ASB that has three aerated runs (17 aerators, total of 1275 HP), and a final quiescent run for secondary effluent treatment. The mill hard pipes condensates to the sewer from the

primary clarifier prior to the ASB. The system was designed with an RT of 16 days. Further details of the treatment system are provided in Figure B3. Three samplings occurred at this mill. Results are presented in Tables B3, B4, and B5. Data for pH, DO, temperature, TSS, and BOD were provided by mill personnel.

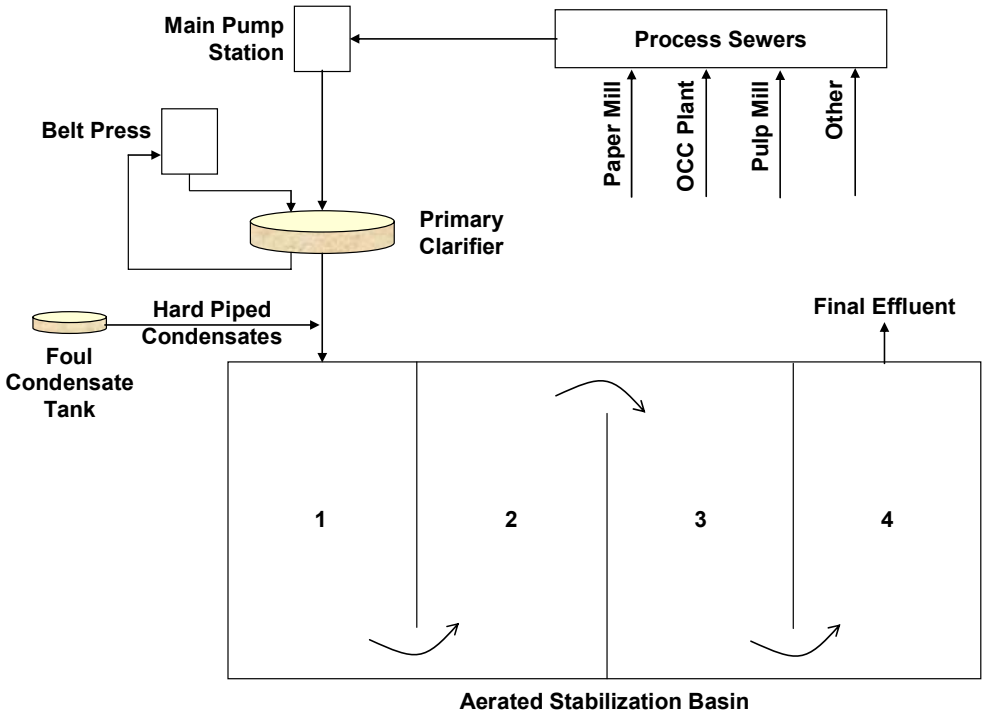

Figure B3. Mill C Wastewater Treatment Plant Schematic

Table B3. Mill C I Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Primary Clarifier Outlet	Front of ASB	Midpoint ASB	Final Effluent	Sludge Dewatering Effluent
Flow (MGD)	8.8	13.2	13.2	13.2	0.46
pH	10.0	8.4	NA	7.3	NA
DO (mg/L)	NA	NA	NA	1.4	NA
Temperature (ºC)	NA	45.8	NA	22.4	NA
TSS (lb/d)	NA	10392	NA	3429	NA
BOD (lb/d)	NA	27517	NA	2007	NA
BOD removal (lb/HP/D)	NA	NA	NA	20	NA
Total sulfide	1310	10800	2810	181	310
MeSH	ND	9260	2370	32.3	ND
DMS	83.5	1430	845	ND	ND
DMDS	ND	2730	1870	ND	ND
DMTS	ND	443	280	ND	ND

NA not applicable; compound not detected in sample

ND not detected above lowest calibration limit: 23.7 µg/L for total sulfide; 31.8 µg/L for MeSH; 38.8 µg/L for DMS; 30.4 µg/L for DMDS; 30.6 µg/L for DMTS

Table B4. Mill C II Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Main Pump Station	Hard Pipe Line	Front of ASB	Midpoint ASB	Final Effluent
Flow (MGD)	8.8	2.0	13.2	13.2	13.2
pH	NA	7.0	9.2	7.4	7.4
DO (mg/L)	NA	NA	1.4	2.0	1.4
Temperature (ºC)	NA	NA	45.8	NA	22.4
Total sulfide	278	12100	12800	6530	54.0
MeSH	ND	2190	5020	910	33.7
DMS	118	2910	3320	570	ND
DMDS	22.6	10000	8280	2000	ND
DMTS	ND	148	112	26.6	ND

NA not applicable; compound not detected in sample

ND not detected above lowest calibration limit: 23.7 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

Table B5. Mill C III Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Main Pump Station	Primary Clarifier Inlet	Primary Clarifier Outlet	Foul Condensate	Hard Pipe Line
Flow (MGD)	8.8	8.8	8.8	NA	4.4
pH	7.4	10.0	10.3	6.9	6.9
DO (mg/L)	NA	NA	NA	NA	NA
Temperature (ºC)	27.4	39.8	37.2	51.8	41.2
Total sulfide	1400	2246	309	55300	38800
MeSH	ND	ND	ND	47300	44300
DMS	ND	ND	ND	524	1890
DMDS	ND	ND	ND	2630	730
DMTS	ND	ND	ND	2750	ND

	Front of ASB	ASB Run #1	ASB Run #2	ASB Run #3	Final Effluent
Flow (MGD)	13.2	13.2	13.2	13.2	13.2
pH	9.4	7.4	7.6	7.6	7.6
DO (mg/L)	0.17	2.2	4.0	3.6	3.9
Temperature (ºC)	38.4	27.3	23.1	22.5	21.1
Total sulfide	11400	226	ND	ND	ND
MeSH	13900	ND	ND	ND	ND
DMS	1570	ND	ND	ND	ND
DMDS	8410	680	ND	ND	ND
DMTS	205	ND	ND	ND	ND

NA not applicable; compound not detected in sample

ND not detected above lowest calibration limit: 23.7 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL D

This kraft mill pulps softwood (pine) and produces about 1200 TPD of bleached pulp using a dissolving kraft process. Average water flow through the treatment system is 43 MGD. The mill is equipped with a primary clarifier followed by an ASB. Flow consists of an alkaline waste stream of 14 MGD that goes through primary clarification, and an acid stream of 27 MGD that enters the waste stream at the mix box. Condensates (2 MGD) are hard piped to the waste stream following the mix box. The first cell of the ASB lagoon consists of 15 acres, is 12 ft deep on average, and contains 25 aerators with a total of 1875 HP. The second cell is also 15 acres and 12 ft deep on average, and contains 11 aerators with a total of 825 HP, for 2700 HP overall. Effluent from these cells flows to a 120 acre lagoon. Further details of the treatment system are provided in Figure B4. Different areas of the treatment plant were sampled during three sampling episodes, and results are shown in Tables B6 and B7. The first sampling event occurred during a low odor time, and the second occurred following an odor event.

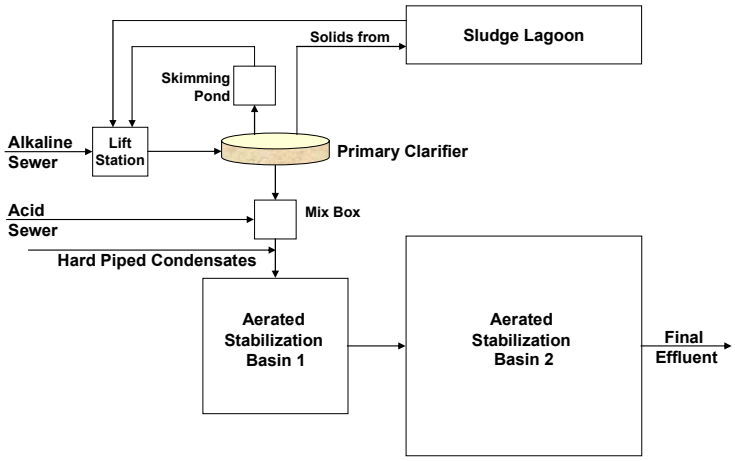

Figure B4. Mill D Wastewater Treatment Plant Schematic

Table B6. Mill D I and II Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Mix Box	Front of ASB	Midpoint ASB	Final Effluent
Mill D I Sampling				
Total sulfide	78.0	1030	446	220
MeSH	31.2	9030	1190	ND
DMS	24.1	4680	1020	ND
DMDS	22.2	587	968	24
DMTS	ND	80.7	24.8	ND
Mill D II Sampling				
Total sulfide	792	66	303	ND
MeSH	24.9	1680	752	24.7
DMS	ND	2580	654	ND
DMDS	ND	1800	1050	ND
DMTS	ND	956	24.8	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

Table B7. Mill D III Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Alkaline Sewer	Acid Sewer	Sludge Lagoon Effluent	Lift Station	Skimming Pond Effluent	Primary Clarifier Outlet
Flow (MGD)	12.4	22.6	2.1	15.1	0.6	15.1
pH	10.7	NA	9.9	NA	9.85	10.5
DO (mg/L)	0.48	NA	0.62	NA	0.56	1.9
Temperature (ºC)	44.4	NA	26.0	NA	28.5	38.1
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	NA	NA	NA	NA	NA	NA
Total sulfide	24700	5470	20900	6560	36000	17000
MeSH	NA	NA	NA	NA	NA	NA
DMS	ND	ND	ND	ND	ND	ND
DMDS	ND	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND

	Hard Pipe Condensate	Mix Box	Front of ASB	ASB Midpoint East Cell	Inlet to Lagoon 2	Final Effluent
Flow (MGD)	3.2	37.7	40.9	40.9	40.9	40.9
pH	NA	6.4	6.3	6.4	6.9	7.2
DO (mg/L)	NA	3.7	0.45	0.45	4.2	2.6
Temperature (ºC)	NA	43.8	45.6	39.8	35.1	26.5
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	NA	NA	NA	NA	NA	NA
Total sulfide	78400	5860	5790	241	89.8	53.6
MeSH	84700	255	5170	261	65.9	NA
DMS	21300	ND	1540	240	40.4	ND
DMDS	9020	ND	2040	1060	223	29.0
DMTS	253	ND	2500	104	ND	ND

NA not available

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL E

Mill E is a kraft and recycle mill that pulps softwood and produces about 1500 TPD of unbleached pulp. Average water flow through the treatment system is 43 MGD. The mill is equipped with a steam stripper for treatment of foul condensates. There are two settling ponds, the second of which is equipped with two injection aerators, followed by an ASB. The treatment system is illustrated in Figure B5. Sample results for RSCs are listed in Table B8.

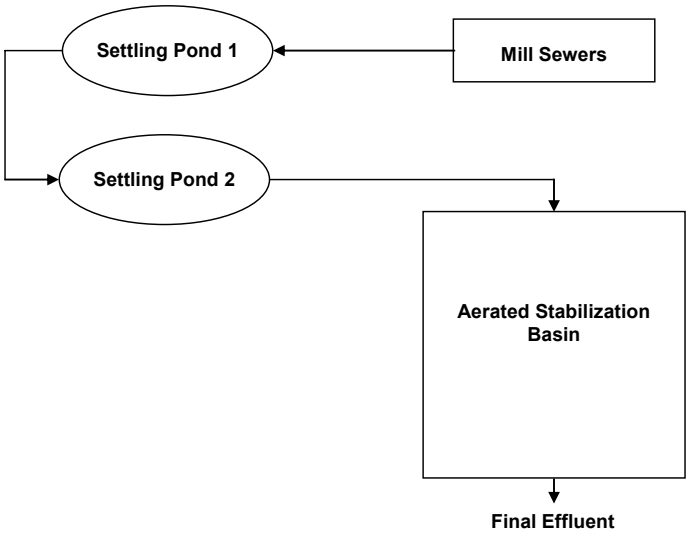

Figure B5. Mill E Wastewater Treatment Plant Schematic

Table B8. Mill E Reduced Sulfur Compound Concentrations (μg S/L)

Compound	Settling Pond 1 Outlet	Front of ASB	Midpoint ASB	Final Effluent
Total sulfide	2670	4500	641	ND
MeSH	26.6	70.2	ND	ND
DMS	22.9	28.7	ND	ND
DMDS	ND	ND	ND	ND
DMTS	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL F

This is a kraft and recycle mill that pulps softwood and produces about 1800 TPD of unbleached pulp. Average water flow through the treatment system is 21 MGD. A stream stripper is used to process foul condensates. The mill is equipped with a primary clarifier followed by a two-stage ASB with twelve 150 HP surface aerators (1800 HP total). The treatment system consists of several waste ponds used for a variety of purposes. This sampling was in support of a project underway by the mill to determine aqueous phase RSC concentrations in selected ponds being monitored for sulfide emissions. Sample results for RSCs are listed in Tables B9 and B10.

Table B9. Mill F Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Pond 17 Outlet	Pond 1 Outlet	Pond 5 Outlet	Pond 8 Outlet
Total sulfide	66900	768	60300	36400
MeSH	ND	ND	ND	81
DMS	ND	ND	ND	ND
DMDS	ND	ND	ND	ND
DMTS	ND	ND	ND	ND

ND not detected above lowest calibration limit: 23.7 μg/L for total sulfide; 31.8 μg/L for MeSH; 38.8 μg/L for DMS; 30.4 μg/L for DMDS; 30.6 μg/L for DMTS

Table B10. Mill F II Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Pond 17 Outlet	Pond 1 Outlet	Pond 5 Outlet	Pond 8 Outlet	Mix Basin
pH	9.68	7.69	9.11	8.9	7.62
DO (mg/L)	3.2	6.8	3.6	2.9	18.5
Temperature (ºC)	18.6	18.1	18.1	18.6	34.8
Specific conductivity (mS/cm)	2.745	2.391	2.757	2.488	2.264
Total sulfide	32900	147	26300	10300	12200
MeSH	ND	ND	ND	41.4	40.4
DMS	ND	ND	ND	ND	20.1
DMDS	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: : 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL G

Mill G is a kraft mill that pulps softwood and hardwood to produce about 1600 TPD of bleached pulp. It is equipped with a steam stripper for treatment of foul condensates. The mill has a primary clarifier followed by a two-stage ASB. ASB 1 is 53 acres with a depth of 11.5 ft and an RT of 10 days. This lagoon contains 14 aerators with a total capacity of 885 HP. The second lagoon consists of two ponds. ASB 2A is 86 acres with an average depth of 9 ft and a total of 1950 HP of aeration. ASB 2B is a 191 acre pond with a depth of 10 to 11 ft, total aeration of 975 HP, and an RT of 12 days. Details of the treatment system are illustrated in Figure B6. Samples were collected from the input to treatment through both ASBs, with the results for RSCs shown in Table B11.

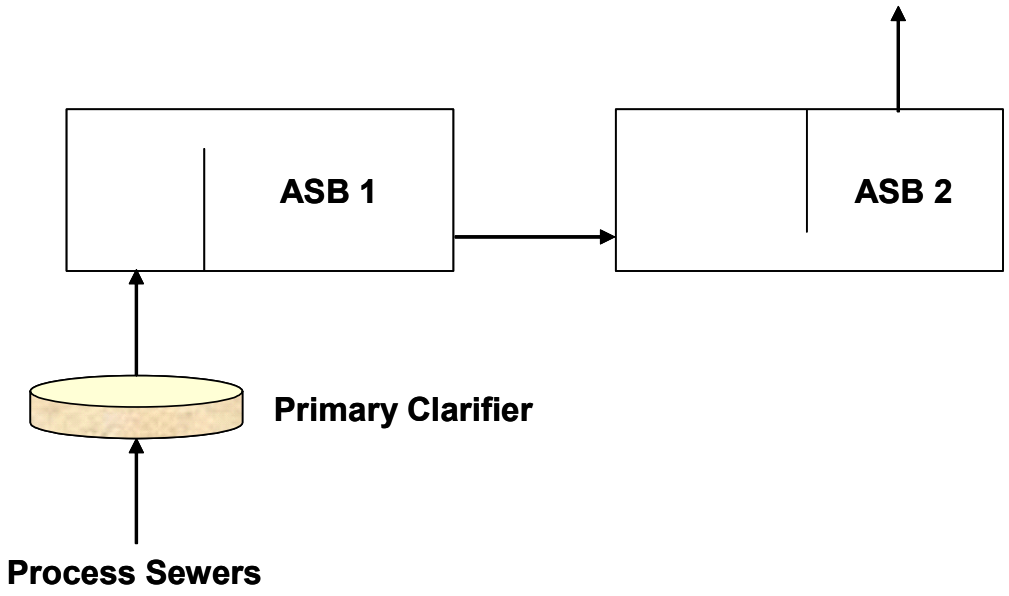

Figure B6. Mill G Wastewater Treatment Plant Schematic

Table B11. Mill G Reduced Sulfur Compound Concentrations (µg S/L)

Compound	Input to ASB	ASB 1 AB Midpoint	ASB 1 AB Effluent	ASB 2AB Midpoint	ASB 2AB Effluent
Total sulfide	19300	146	194	854	56.0
MeSH	282	38.5	57.6	33.9	ND
DMS	116	ND	ND	ND	ND
DMDS	303	ND	ND	ND	ND
DMTS	32.8	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL H

This is a kraft and recycle mill that pulps softwood, hardwood, and recycled fiber to produce about 1600 TPD of bleached and unbleached pulp. Average water flow through the treatment system is 26 MGD. The mill utilizes steam stripping and also hard pipes some foul condensates. The hard pipe inlet is at the front of the ASB. The mill is equipped with a 250 ft diameter primary clarifier followed by a 75 acre ASB with a design volume of 303 MG, equipped with 53 aerators with a total of 3975 HP and a 300 HP fine bubble diffused air system. The current RT is approximately 4 days. Flow from the ASB is directed to a 20 acre, 50 MG pond. This pond has a theoretical residence time of 1 day. Wastewater then flows to a 43 acre, 82 MG hold and release basin equipped with five surface aerators. The system generally operates at a 93% BOD removal efficiency. Details of the treatment system are illustrated in Figure B7. Samples were collected from different areas of the condensate and treatment system during two separate sampling episodes, with the results listed in Table B12.

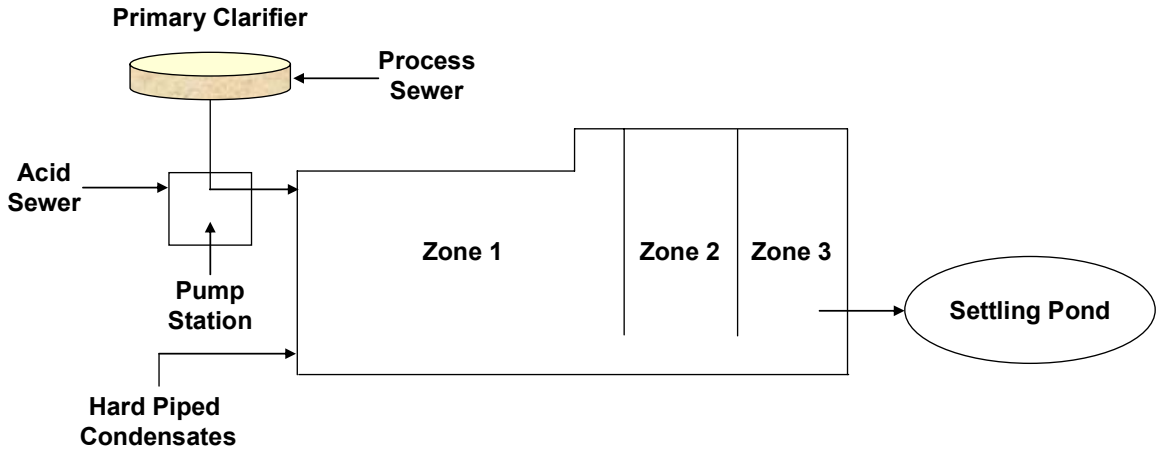

Figure B7. Mill H Wastewater Treatment Plant Schematic

Table B12. Mill H Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Influent to ASB	Zone 1 across ASB	Zone 2 across ASB	Zone 3 across ASB	ASB Effluent	Settling Pond Effluent
Flow (MGD)	26.5	26.5	26.5	26.5	26.5	26.5
Temperature (ºC)	53.3	NA	NA	NA	32.2-35	29.4-31
Mill H I sampling						
Total sulfide	397	16900	29200	20900	224	149
MeSH	2420	ND	ND	ND	ND	ND
DMS	3060	ND	ND	26.3	ND	173
DMDS	377	ND	ND	ND	ND	ND
DMTS	51.2	ND	ND	ND	ND	ND
Mill H II sampling						
Total sulfide	61.7	21700	30000	24000	97.8	73.5
MeSH	175	ND	ND	ND	ND	ND
DMS	2670	ND	ND	ND	ND	119
DMDS	619	ND	ND	ND	ND	ND
DMTS	318	ND	ND	ND	ND	ND

NA not available

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL I

Production capacity at Mill I is approximately 475,000 ton per year of unbleached kraft pulp. The mill produces kraft paper and lightweight linerboard. A schematic of the WWTP is provided in Figure B8. The mill utilizes steam stripping and also hard pipes some foul condensates. Effluent from the pulp and paper mill enters the primary clarifier with a combined average flow of 14.7 MGD. Effluent from the primary clarifier is routed to the inlet of a 21.5 acre aeration basin equipped with 1605 HP of aeration and 425 HP of sub-surface aeration. RT in the ASB is approximately 3.8 days. Effluent flows through a spillway to the 60 acre stabilization basin No.1, a single cell pond with an RT of approximately 5 days. Effluent from the first stabilization pond flows into a two cell, 190 acre stabilization pond with an additional 16 day RT. Effluent from the second stabilization pond enters a single cell, 120 acre stabilization pond with a 10 day RT. Samples were collected from the inlet, within, and outlet of the primary clarifier, condensate hard pipe, across the ASB, the retention pond, and the emergency pond. Average results of these analyses are listed in Table B13.

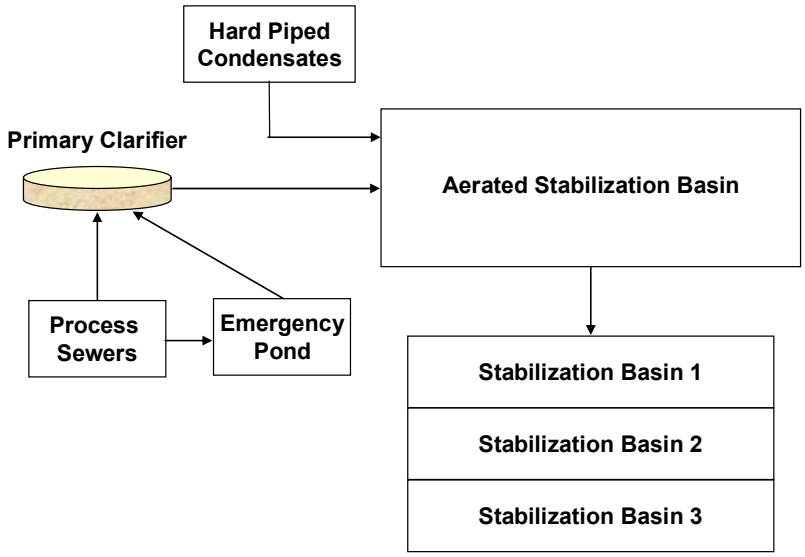

Figure B8. Mill I Wastewater Treatment Plant Schematic

Table B13. Mill I Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	Condensate Hard Pipe	ASB Outlet	Stabilization Basin 1 Outlet
Total sulfide	617	466	102000	ND	40.9
MeSH	I	I	44100	ND	ND
DMS	19.9	22.6	3680	ND	ND
DMDS	ND	ND	2490	ND	ND
DMTS	ND	ND	374	ND	ND

NA not available
I interference
ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL J

Mill J is a kraft, neutral sulfite semi-chemical (NSSC), and recycle mill that pulps softwood and hardwood and performs nondeink recycling of OCC to produce about 1800 TPD of unbleached pulp. Average water flow through the treatment system is 22.5 MGD. Foul condensates are currently hard piped to the treatment lagoon. The mill is equipped with a 160 ft diameter primary clarifier followed by three equalization ponds in series. The first pond contains four 75 HP aerators, the second and third ponds each contain two 75 HP aerators. These ponds discharge to ASB1, equipped with eight 40 HP aerators and two 75 HP aerators, which discharges to ASB2, equipped with sixteen 75 HP aerators and one 40 HP aerator. Pulp mill effluent enters the system at the front of ASB1 and the hard piped condensate inlet is located at the front of ASB2. The treatment system has an overall RT of 7 days and is diagramed in Figure B9.

Samples from this facility were collected several times during this and other NCASI projects. One project involved an assessment of odorous compounds throughout the treatment system, and another focused on reducing odor related to total sulfide in the primary clarifier and equalization ponds at the front of the WWTP. RSC results for the various samplings are listed in Tables B14, B15, and B16.

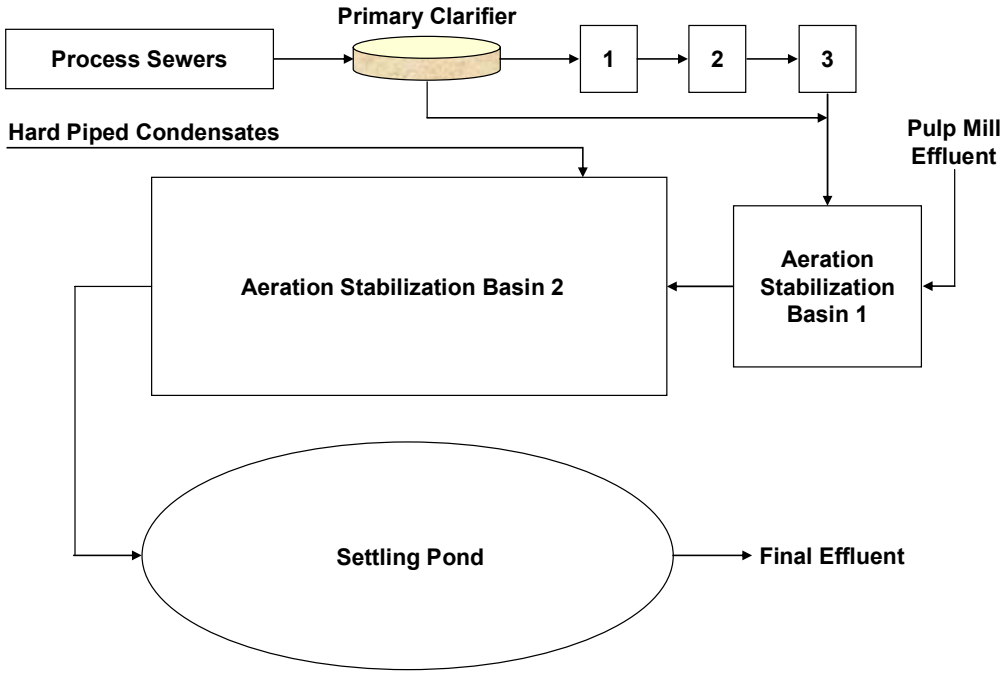

Figure B9. Mill J Wastewater Treatment Plant Schematic

Table B14. Mill J I Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	Recaust. Sewer	EP 1 Outlet	EP 2 Outlet	EP 3 Outlet
Flow (MGD)	10.14	9.44	0.03	4.72	4.72	4.75
pH	7	7	NA	7	7	7
DO (mg/L)	3	0.42	NA	0.2	0.5	0.28
Temperature (ºC)	46	44.6	NA	36.4	32.5	34
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	72400	50200	100	NA	NA	23300
BOD removal (lb/HP/D)	NA	NA	NA	NA	NA	44.8
COD (ppm)	1640	1216	NA	NA	NA	1144
Total sulfide	406	12600	75400	1690	17300	24400
MeSH	ND	37.3	ND	ND	53	68.8
DMS	ND	34.6	ND	ND	ND	ND
DMDS	ND	25.2	ND	ND	ND	ND
DMTS	ND	29.1	ND	ND	ND	ND
Total sulfur	172	132	653	167	155	136
	Pulp Mill Effluent	ASB1 Outlet	Foul Condensate	ASB2 Midpoint	ASB2 Outlet	Final Effluent
Flow (MGD)	0.98	10.45	0.43	10.88	10.88	10.88
pH	9	7	NA	7	7	7
DO (mg/L)	0.14	1.74	NA	0.56	5.45	0.92
Temperature (ºC)	41	28.5	NA	24.3	22.3	22.4
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	5200	16400	NA	NA	4900	4100
BOD removal (lb/HP/D)	NA	NA	NA	NA	9.3	20
COD (ppm)	1184	910	NA	NA	583	563
Total sulfide	14200	3070	75500	201	112	82.0
MeSH	ND	ND	5390	ND	ND	ND
DMS	ND	ND	990	ND	ND	ND
DMDS	ND	ND	1760	ND	ND	ND
DMTS	ND	ND	176	ND	ND	ND
Total sulfur	86	145	57	141	141	136

NA not available

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

Table B15. Mill J II Reduced Sulfur Compound (µg S/L) and Sulfate, Thiosulfate, and Sulfite (mg/L) Concentrations

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	Recaust. Sewer	Outlet of EP 1	Outlet of EP 2	Outlet of EP 3
Flow (MGD)	10.48	9.83	0.02	6.88	6.88	6.90
pH	7.5	6.0	NA	7.7	7.5	7.8
DO (mg/L)	2.2	0.93	NA	0.2	0.16	0.24
Temperature (ºC)	42.8	42.3	NA	35.7	32.5	30
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	86400	53300	NA	NA	NA	28200
Total sulfide	252	8920	443000	1740	19900	7430
MeSH	139	210	NA	NA	NA	NA
DMS	ND	ND	ND	ND	ND	ND
DMDS	ND	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND
Sulfate	390	390	1000	470	480	490
Thiosulfate	<5	<5	640	9	17	15
Sulfite	<5	<5	200	<5	<5	<5
	EP Sump	ASB1 Outlet	Foul Condensate	ASB 2 Midpoint	ASB 2 Outlet	Final Effluent
Flow (MGD)	9.85	10.93	0.45	11.37	11.37	11.37
pH	8	8.6	NA	7.5	7.6	7.5
DO (mg/L)	0.27	0.16	NA	0.98	3.44	1.22
Temperature (ºC)	33.8	28.9	NA	25.5	22.8	22.4
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	NA	18900	NA	NA	6100	5100
Total sulfide	7880	3730	44300	292	ND	ND
MeSH	NA	NA	2470	ND	ND	ND
DMS	ND	ND	870	ND	ND	ND
DMDS	ND	ND	548	ND	ND	ND
DMTS	ND	ND	127	ND	ND	ND
Sulfate	470	520	<5	540	500	480
Thiosulfate	15	<5	<5	<5	<5	<5
Sulfite	<5	<5	<5	<5	<5	<5

NA not available

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

Table B16. Mill J III Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	EP 1 Outlet	EP 2 Outlet
Flow (MGD)	9.7	9.1	3.64	3.64
pH	7.9	6.5	7.7	7.5
DO (g/L)	2.2	1.4	1.3	2.7
Temperature (ºC)	45.0	438	27.8	25.6
TSS (lb/d)	NA	NA	NA	NA
BOD (lb/d)[a]	66200	51200	NA	NA
Total sulfide	57.3	5490	ND	ND
MeSH	NA	NA	NA	NA
DMS	NA	NA	NA	NA
DMDS	NA	NA	NA	NA
DMTS	NA	NA	NA	NA
	EP 3 Outlet	EP Outlet and Clarifier Outlet	Pulp Mill Effluent	ASB1 Outlet
Flow (MGD)	3.64	9.1	2.2	11.3
pH	7	7	10.4	7.9
DO (g/L)	4.9	4.6	NA	NA
Temperature (ºC)	25.4	25.8	37.5	29.5
TSS (lb/d)	NA	NA	NA	NA
BOD (lb/d)[a]	35000	NA	6500	26400
Total sulfide	2970	2920	4870	1950
MeSH	NA	123	NA	NA
DMS	NA	ND	NA	NA
DMDS	NA	ND	NA	NA
DMTS	NA	ND	NA	NA

[a] data from monthly average April 2004

NA not analyzed for in sample

ND not detected above lowest calibration limit: 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL K

Mill K is a kraft mill that pulps softwood and hardwood to produce from 2000 to 2500 TPD of bleached pulp. Average water flow through the treatment system (Figure B10) is 50 MGD. At the time samples were collected, foul condensates were hard piped to the front of ASB 1. The mill is equipped with a 230 ft diameter primary clarifier (RT 2 to 3 hours) followed by a 5 acre equalization pond that is not aerated. The combined bleach plant sewer enters the waste stream at the equalization pond. The combined flow then goes ¼ mile via an open canal to the ASB. The ASB is made up of three aerated lagoons encompassing 250 acres. ASB 1 (43.5 acres, 2000 ft by 900 ft, 8 ft depth) contains sixteen 60 and 75 HP aerators (990 HP total). ASB 2 (74.2 acres, 2100 ft by 1500 ft, 8 ft depth, RT 1 day) contains eighteen 60 HP aerators. ASB 3 (122 acres, 2650 ft by 1000 ft, 8.5 ft depth, RT 6 days) contains nineteen 60 HP aerators. The system averages 3500 HP overall. This system is followed by a quiescent pond of approximately 300 acres. RT is 14 days. Several samplings were conducted during odor reduction studies. RSC results for WWTP surveys are provided in Tables B17 and B18.

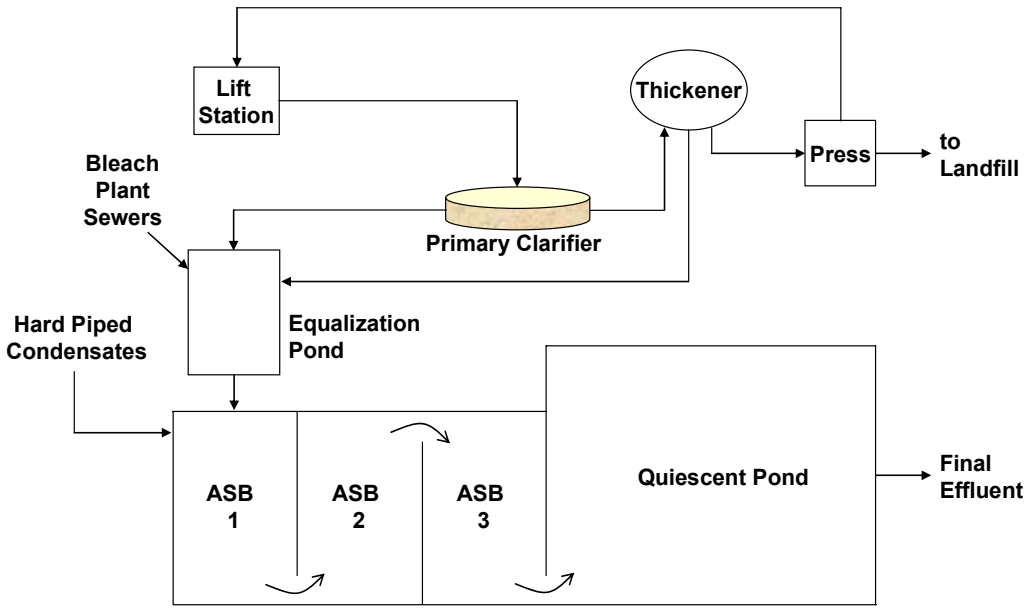

Figure B10. Mill K Wastewater Treatment Plant Schematic

Table B17. Mill K I and II Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	Hard Pipe Condensate	ASB 1 Inlet	ASB 1 Outlet
Mill K I					
Total sulfide	NS	15800	132000	4540	18800
Mill K II					
Total sulfide	14250	13000	NS	13300	18000
MeSH	6560	370	NS	2720	875
DMS	554	139	NS	1330	383
DMDS	2620	546	NS	935	91
DMTS	170	80.3	NS	171	56.1

NS not sampled

ND not detected above lowest calibration limit: 22.3 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

Table B18. Mill K III Parameters and Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Process Sewer 1	Process Sewer 2	Primary Clarifier Outlet	Bleach Plant Sewer	Equalization Pond	A1 Canal to ASB
Flow (MGD)	7.7	NA[a]	37.5	12.5	50	50
pH	NA	NA	9	3	NA	6.9
BOD removal/HP/d[b]	NA	NA	NA	NA	NA	NA
K V Concentrations (μg S/L)						
Total sulfide	36000	16200	5260	50.2	1320	1220
MeSH	10500	1970	2070	503	612	578
DMS	643	ND	126	330	276	244
DMDS	8250	45.2	186	585	206	161
DMTS	487	ND	60.1	ND	81.2	86.5
K VI Concentrations (μg S/L)						
Total sulfide	NA	6680	22900	ND	5930	6270
MeSH	NA	424	2490	ND	1800	3310
DMS	NA	273	243	ND	181	212
DMDS	NA	4550	2710	120	1580	539
DMTS	NA	264	470	ND	125	405
	Hard Piped Condensate	ASB 1 Outlet	ASB 2 Outlet	ASB 3 Outlet	Quiescent Pond	Final Effluent
Flow (MGD)	3	53	53	53	53	53
pH	9.3	7.1	6.9	7.4	7.4	NA
BOD removal/HP/d[b]	NA	61	52	20	NA	NA
K V Concentrations (μg S/L)						
Total sulfide	96100	15500	318	63.2	28.0	ND
MeSH	99700	1520	133	35	42.3	43.6
DMS	21200	280	37.0	ND	ND	ND
DMDS	12700	137	71.9	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND
K VI Concentrations (μg S/L)						
Total sulfide	133000	14364	4150	NA	ND	NA
MeSH	151000	2910	964	NA	221	NA
DMS	21900	383	99.3	NA	ND	NA
DMDS	5750	212	62.2	NA	ND	NA
DMTS	694	ND	31.1	NA	ND	NA

[a] flow data not provided for this location

[b] data from 8 month average, 2003

NA not analyzed

ND not detected above lowest calibration limit: 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL L

This is a recycle (40 to 45%)/TMP (55 to 60%) mill that produces about 450 TPD of directory paper. It utilizes about 6% purchased kraft pulp. Pulp bleaching and brightening uses hydrosulfite as well as hydrogen peroxide with a little hypochlorite. Average water flow through the treatment system (Figure B11) is 8 MGD. The mill is equipped with primary clarification (1.9 MG volume, 21,382 ft^2, RT 5.4 hours) followed by an AS system consisting of a 2.2 MG aeration tank containing ten 40 HP surface aerators with an RT of 4.4 hours, and a secondary clarifier with a volume of 1.2 MG, an area of 13,273 ft^2, and an RT of 2.4 hours. The system has 400 HP of aeration in all and an overall RT of 12.2 hours. Primary and secondary sludge are dewatered by screw presses. RSC samples were collected throughout the WWTP. Sampling sites and analytical results are shown in Table B19.

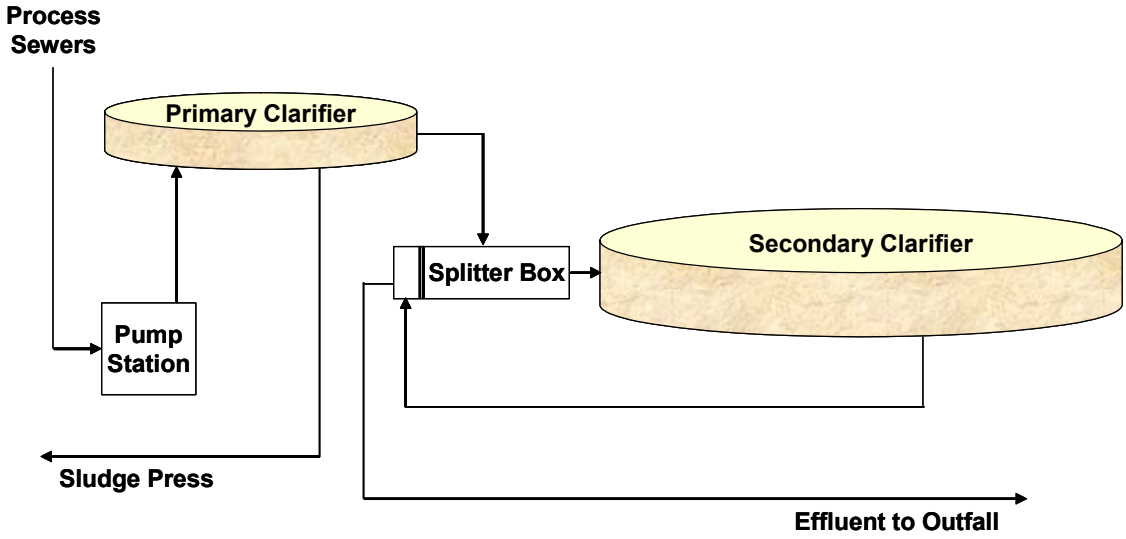

Figure B11. Mill L Wastewater Treatment Plant Schematic

Table B19. Mill L Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Paper Machine Sewer	Recycle Plant Sewer	Screw Press Filtrate	Main Pump Station
Flow (MGD)	5.5	1.88	0.5	8.46
pH	5.42	7.72	7.12	6.99
DO (mg/L)	NA	8.0	7.4	7.1
Temperature (ºC)	35	42	31	36
TSS (lb/d)[a]	NA	NA	NA	156355
BOD (lb/d)[a]	NA	NA	NA	24143
Total sulfide	ND	ND	995	ND
MeSH	ND	ND	74.2	ND
DMS	ND	ND	ND	ND
DMDS	ND	ND	ND	ND
DMTS	ND	ND	ND	ND
	Primary Clarifier Outlet	Aeration Basin Front	Aeration Basin Midpoint	Final Effluent
Flow (MGD)	8.46	8.46	8.46	8.46
pH	6.61	7.14	7.07	7.27
DO (mg/L)	3.5	2.2	2.2	5.4
Temperature (ºC)	36	34	31	30
TSS (lb/d)[a]	4703	NA	NA	2035
BOD (lb/d)[a]	11237	NA	NA	764
Total sulfide	5039	4013	2725	ND
MeSH	133	28.4	ND	ND
DMS	ND	ND	ND	ND
DMDS	ND	ND	ND	ND
DMTS	ND	ND	ND	ND

[a] data provided by mill for March 2004 monthly average

NA not analyzed

ND not detected above lowest calibration limit: 20 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL M

Mill M is an NSSC/recycled fiber mill that produces about 2320 TPD of corrugated medium. The mill does not have a bleach plant. Average water flow through the treatment system is 7 MGD. The mill is equipped with primary clarification followed by an ASB and an activated sludge unit (ASU) with secondary clarification. Condensates are currently hard piped to the ASB prior to the ASU. Further details of the treatment system are provided in Figure B12. RSC results are shown in Table B20.

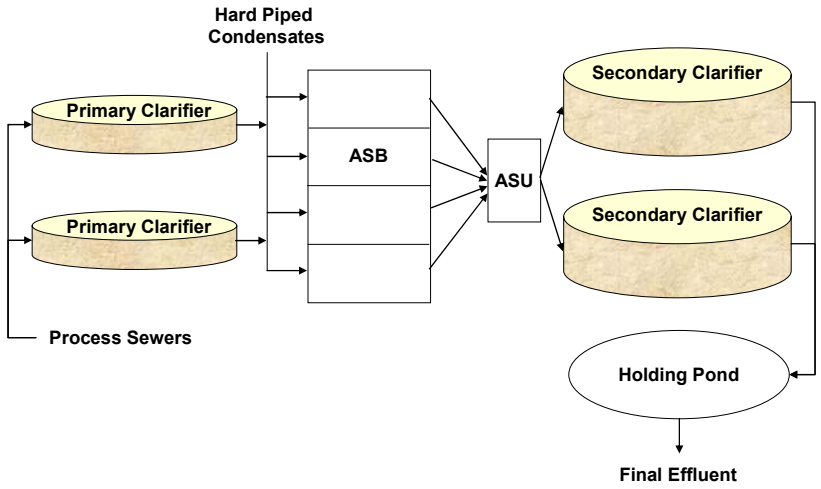

Figure B12. Mill M Wastewater Treatment Plant Schematic

Table B20. Mill M Reduced Sulfur Compound Concentrations (µg S/L)

Sampling Location	Total Sulfide	MeSH[a]	DMS	DMDS	DMTS
Mill process effluent	414	NA	19.9	ND	ND
Screw press filtrate	17100	132	227	ND	ND
Inlet to primary clarifiers	1287	NA	36.5	28.3	ND
#1 Primary clarifier outlet	1810	NA	154	ND	ND
#2 Primary clarifier outlet	2140	NA	87.6	ND	ND
Inlet to ASB	2505	NA	113	ND	ND
Hard piped condensate	95700	18400	25.9	1760	128
ASB pond 1 outlet	545	NA	ND	ND	ND
ASB pond 2 outlet	412	NA	ND	ND	ND
ASB pond 3 outlet	3289	NA	ND	81.4	ND
ASB pond 4 outlet	465	NA	ND	ND	ND
ASU outlet	693	NA	ND	ND	ND
#1 Secondary clarifier outlet	262	NA	ND	ND	ND
#2 Secondary clarifier outlet	197	NA	ND	ND	ND
2nd Clarifier underflow	583	NA	ND	ND	ND
Sludge pond outlet	83000	51.3	27.3	ND	ND
2nd Clarifier overflow	5370	NA	ND	ND	ND

[a] some results not available (NA) due to interference from sulfur dioxide

ND not detected above lowest calibration limit: 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL N

This is a bleached kraft mill producing approximately 660 TPD of pulp. Average water usage is 51,000 m^3/day. The mill runs softwood and hardwood lines. The WWTP receives effluent from a municipal sewage treatment plant that undergoes tertiary treatment in the mill's secondary treatment system. The WWTP consists of primary clarifiers, an equalization basin, and an AS system (Figure B13). Condensates are currently hard piped to the WWTP at the second ASB. Sampling focused on final effluent and hard piped condensates, and results are shown in Table B21.

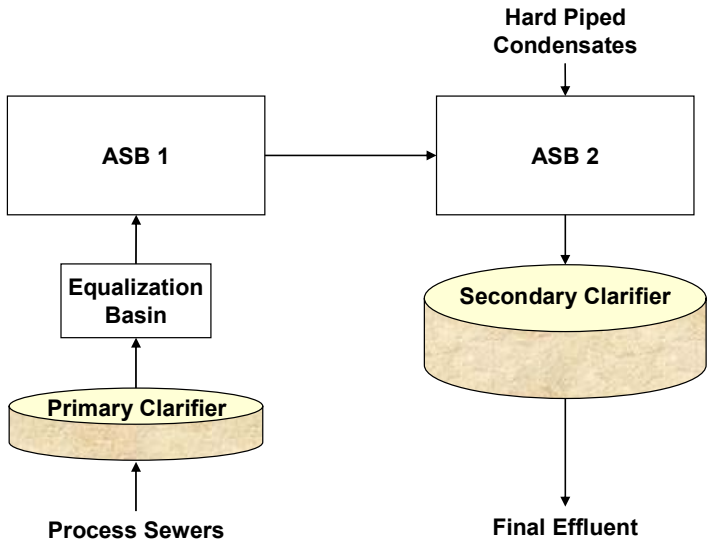

Figure B13. Mill N Wastewater Treatment Plant Schematic

Table B21. Mill N Reduced Sulfur Compound Concentrations (μg S/L)

Compound	Final Effluent	Hard Piped Condensate
Total sulfide	ND	26100
MeSH	ND	70700
DMS	ND	16800
DMDS	ND	1920
DMTS	ND	218

ND not detected above lowest calibration limit: 19.6 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL O

This kraft mill produces approximately 1350 MTPD of bleached kraft pulp from softwood (pine and fir). Average water flow through the treatment system is 115,000 m^3/day. The mill is equipped with primary clarification followed by two settling ponds and an ASB. The ASB has 31 surface aerators that provide a total of 2325 HP across the basin (Figure B14) and a submerged jet injecting oxygen at the front of the ASB. ASB discharge averages a total BOD_5 of 22 mg/L with soluble BOD of 8 mg/L and TSS of 18 mg/L. The mill utilizes steam stripping and treats some foul condensates in the WWTP. The treatment system was surveyed twice to assess RSCs, yielding the results in Table B22.

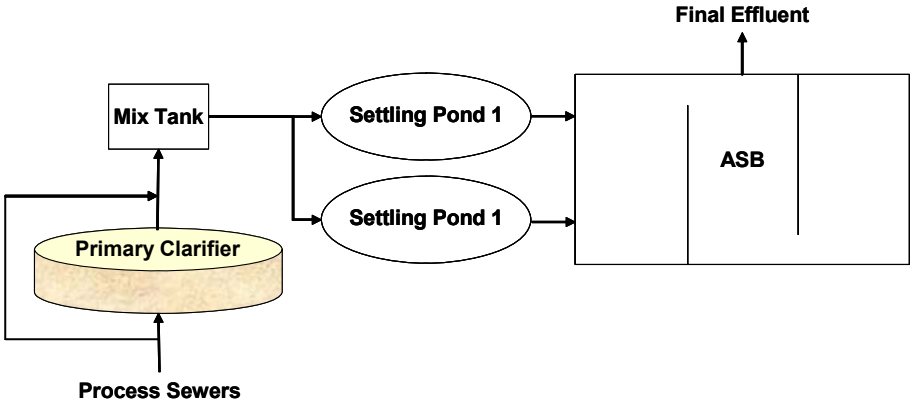

Figure B14. Mill O Wastewater Treatment Plant Schematic

Table B22. Mill O Reduced Sulfur Compound Concentrations (µg S/L)

Sampling Location	Total Sulfide	MeSH	DMS	DMDS	DMTS
Mill O I					
Primary clarifier inlet	113	ND	87.3	149	ND
Primary clarifier outlet	57	37.6	75.6	62.7	ND
Settling pond inlet	ND	ND	ND	46.7	ND
ASB inlet	310	ND	34.1	27.6	ND
ASB section 1 midpoint	57	ND	20.4	ND	ND
ASB section 1 outlet	85	ND	24.5	ND	ND
ASB section 2 outlet	70	ND	26.1	ND	ND
ASB section 3 outlet	39	ND	ND	ND	ND
Final effluent	ND	ND	ND	ND	ND
Mill O II					
Primary clarifier inlet	64.5	ND	61.5	78.8	ND
Primary clarifier outlet	ND	ND	72.2	39.5	ND
Settling pond inlet	58.3	ND	25.9	30.4	ND
ASB inlet	188	ND	31.4	ND	ND
ASB section 1 midpoint	108	ND	24.7	ND	ND
ASB section 1 outlet	89.9	ND	20.6	ND	ND
ASB section 2 outlet	80.1	ND	ND	ND	ND
ASB section 3 outlet	80.8	ND	ND	ND	ND
Final effluent	62.8	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL P

This bleached kraft mill pulps softwood at a capacity of approximately 363,000 tons per year (TPY). A schematic of the WWTP is provided in Figure B15. The mill is equipped with a steam stripper to process foul condensates. The alkaline sewer is routed to the primary clarifier at a flow rate of approximately 11.7 MGD. Effluent from the primary clarifier is mixed with the acid sewer, landfill leachate, and solids dewatering flow from the screw press. The mixed effluent is routed to a four zone, 50 acre aeration pond with a combined flow of 16.7 MGD and equipped with 1275 HP of aeration. Flow from the first pond enters a second ASB utilizing 350 HP in two zones, and approximately 9.2 MGD from the second zone are pumped back to the point where the acid and

alkaline streams mix. Effluent from the second ASB enters a 116 acre stabilization pond, followed by a discharge canal that has 80 HP of surface aeration. Samples were collected from the primary clarifier inlet, primary clarifier outlet, ASB inlet, and ASB outlet. Several samples were collected at some of these sites over a three day period and the results listed in Table B23 represent the averages of those measurements.

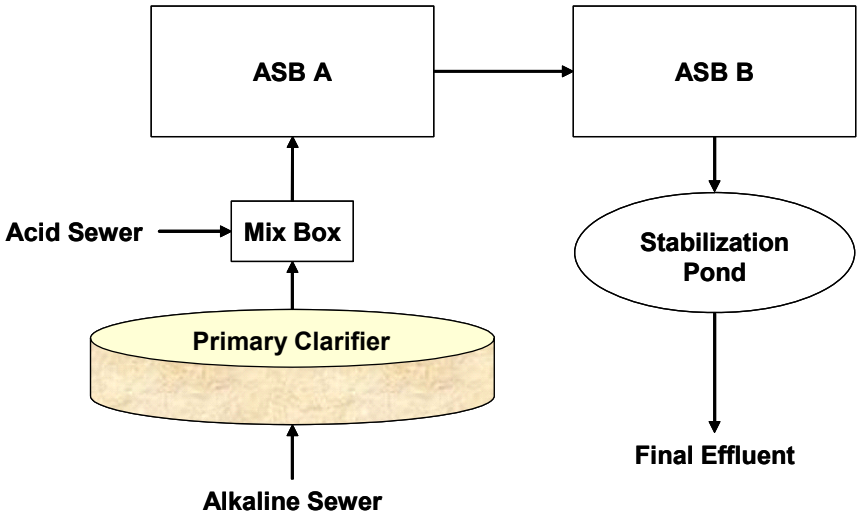

Figure B15. Mill P Wastewater Treatment Plant Schematic

Table B23. Mill P Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Primary Clarifier Inlet (n = 8)	Primary Clarifier Outlet (n = 8)	ASB Inlet (n = 10)	ASB Outlet (n = 5)
Total sulfide	526	637	417	290
MeSH	56.0	86.0	134	49.0
DMS	37.0	34.0	42.0	29.0
DMDS	840	431	217	13.0
DMTS	22.0	94.0	43.3	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL Q

Total production at Mill Q is 748,000 TPY of bleached kraft, with 456,000 tons from softwood and 292,000 tons from hardwood, both from continuous digesters. The mill utilizes a steam stripper to treat foul condensates. The bleach plants associated with the two pulping lines use oxygen delignification and produce 594,000 TPY of bleached paper and 292,000 TPY of recycled liner board. Wastewater enters the WWTP (Figure B16) through either of two 32 acre settling ponds. Approximately 38 MGD of flow enters secondary treatment at a four cell, 67 acre ASB with 3550 HP of aeration. Wastewater then cascades over a riffle to a 39 acre retention pond followed by a 169 acre retention pond. Samples were collected across both settling ponds and across the ASB. The results of these analyses are listed in Table B24.

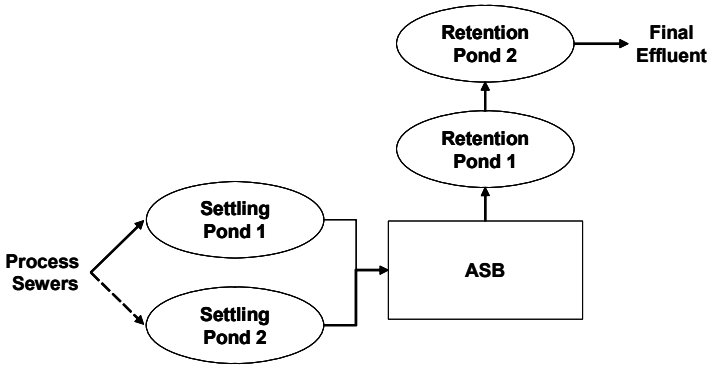

Figure B16. Mill Q Wastewater Treatment Plant Schematic

Table B24. Mill Q Average Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Settling Pond 1 Inlet (n=6)	Settling Pond 1 Outlet (n=4)	Settling Pond 2 Inlet (n=8)	Settling Pond 2 Outlet (n=5)	ASB Inlet (n=7)	ASB Outlet (n=5)
Total sulfide	654	1829	335	1020	2847	221
MeSH	ND	23.5	51.1	21.4	27	ND
DMS	19.4	22.0	60.7	24.5	25	ND
DMDS	30.9	34.7	61.9	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL R

Mill R produces 258,000 MTPY of bleached softwood kraft and 406,000 MTPY of bleached hardwood kraft. This mill uses a stream stripper to process foul condensates. The process sewers (25 MGD) go through a bar screen and then into two 180 ft primary clarifiers (12.5 MGD) with RTs of about 4 hours each. The process sewer consists of pulp mill effluent, alkaline sewer, evaporator effluent, powder and recovery area sewers, and the causticizing area sewer. Effluent from the clarifiers goes to the mix box, where 5 to 6 MGD of acid sewer from the bleach plants and about 20,000 GD of a sanitary sewer are added. From the mix box it moves through a splitter box into two ASBs. These consist of two cells, each equipped with nine 75 HP aerators. From the ASBs the wastewater flows to a final settling basin. Samples were collected from the mix box, as well as from the inlet and outlet of the ASB. The results of these analyses are listed in Table B25.

Table B25. Mill R Average Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Mix Box (n=1)	ASB1 Inlet (n=3)	ASB1 Outlet (n=3)	ASB2 Inlet (n=3)	ASB2 Outlet (n=3)
Total sulfide	75.7	70.6	ND	306	ND
MeSH	ND	ND	19.6	ND	ND
DMS	ND	ND	ND	ND	ND
DMDS	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL S

Mill S is an unbleached kraft mill producing 821,470 MTPY: 27% specialties, 35% kraft board, and 37% linerboard. Furnish is approximately 25% hardwood and 75% softwood. The mill is equipped with a steam stripper to process foul condensates. Wastewater is treated using primary clarification with oxygen injection followed by AS (Figure B17). Samples were collected during two different sampling events from the forced main prior to the clarifier, primary clarifier center well, primary clarifier outlet, inlet to the aeration basin, and outlet from the aeration basin. Average results for three samples collected throughout the day are listed in Table B26 for the first sampling episode. Average results (n=12) of the RSC analyses, oxidation reduction potential, pH, and temperature for the second sampling episode are shown in Table B27.

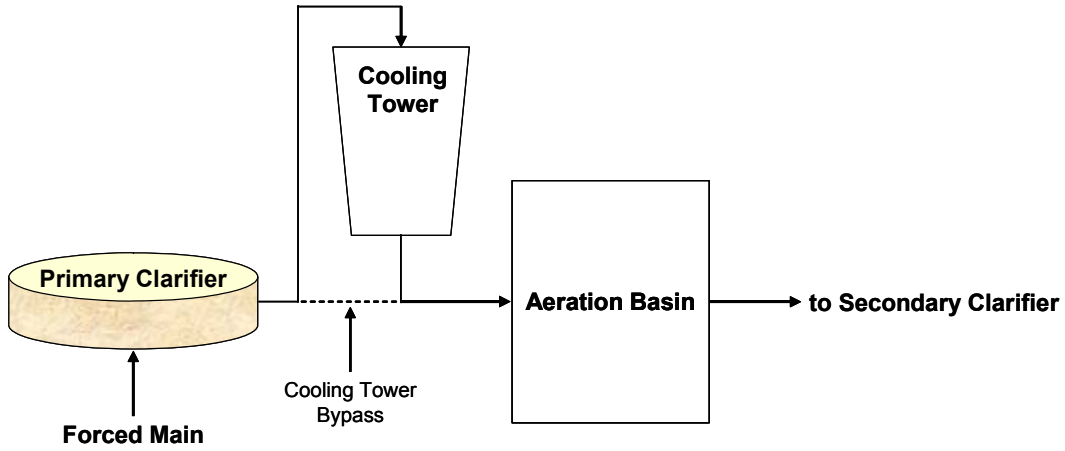

Figure B17. Mill S Wastewater Treatment Plant Schematic

Table B26. Mill S Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Forced Main	Primary Clarifier Center Well	Primary Clarifier Outlet	Aeration Basin Inlet	Aeration Basin Outlet
Total sulfide	1778	4793	15520	12567	69.0
MeSH	1011	972	3960	3753	120
DMS	63	66.0	80.0	77.0	ND
DMDS	2650	2350	289	231	ND
DMTS	319	278	74.0	185	ND

ND not detected above lowest calibration limit: 30 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

Table B27. Mill S Oxidation Reduction Potential, pH, Temperature, and Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Forced Main	Primary Clarifier Center Well	Primary Clarifier Outlet	Aeration Basin Inlet	Aeration Basin Outlet
ORP	-184	-128	-90	-182	119
pH	8.9	9.0	7.8	8.1	7.5
Temperature (ºC)	41	39	37	35	33
Total sulfide	2346	1215	2636	1171	55
MeSH	83	146	466	235	ND
DMS	83	79	66	28	ND
DMDS	1446	1102	479	188	ND
DMTS	114	113	111	94	ND

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL T

This mill produces approximately 348,500 TPY of air dried pulp consisting of 90% hardwood and 10% softwood bleached kraft. A schematic of the WWTP is provided in Figure B18. The primary clarifier is charged with 8.2 MGD of pulp mill cooling water, 6.1 MGD from the paper mill and coater (non-contact cooling), and smaller amounts from the debarker, pulp drier (non-contact cooling), lime kiln, carbon pit, and stormwater. After primary clarification, effluent is mixed with about 0.14 MGD of sanitary water, 1.2 MGD from the mud ash lagoon, and effluent from the pulp mill bleach pit prior to the mixing chamber. Recovered water from the evaporators and turpentine condensates are treated with peroxide in static mixers and added to the WWTP at the first ASB. ASB 1 (36.8 acres) is followed by a second ASB (25.1 acres) that flows into a 118.8 acre stabilization lagoon prior to final outfall. Samples were collected at the mix box, ASB inlet, and final effluent for three days. Average results of these analyses are listed in Table B28.

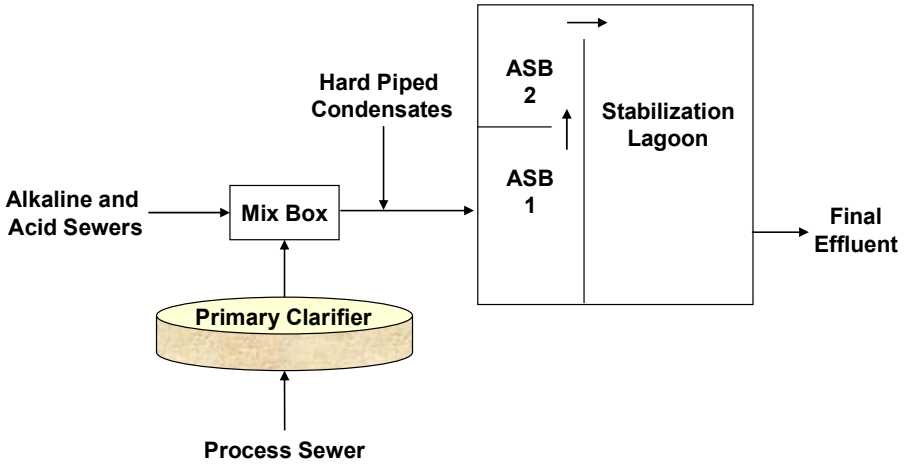

Figure B18. Mill T Wastewater Treatment Plant Schematic

Table B28. Mill T Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Mix Box	Aeration Basin Inlet	Aeration Basin Outlet
Total sulfide	3480	2160	31.4
MeSH	532	605	ND
DMS	541	838	68.1
DMDS	511	1806	110
DMTS	134	177	ND

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL U

Mill U produces 200,000 MTPD of air dried hardwood kraft and 190,000 MTPD of softwood kraft. Mill production is 7.4% uncoated freesheet, 11.4% specialties, and 81.2% kraft pulp. The wastewater treatment system (Figure B19) consists of two primary settling ponds that are switched back and forth to allow further settling. After settling, the effluent enters an aeration basin that contains two cells with a pinch at about 45% of the total area. Effluent then enters a quiescent basin for final treatment. Samples were collected throughout the south settling basin, ASB cell 1, ASB cell 2, the quiescent basin, and final effluent. Results are listed in Table B29.

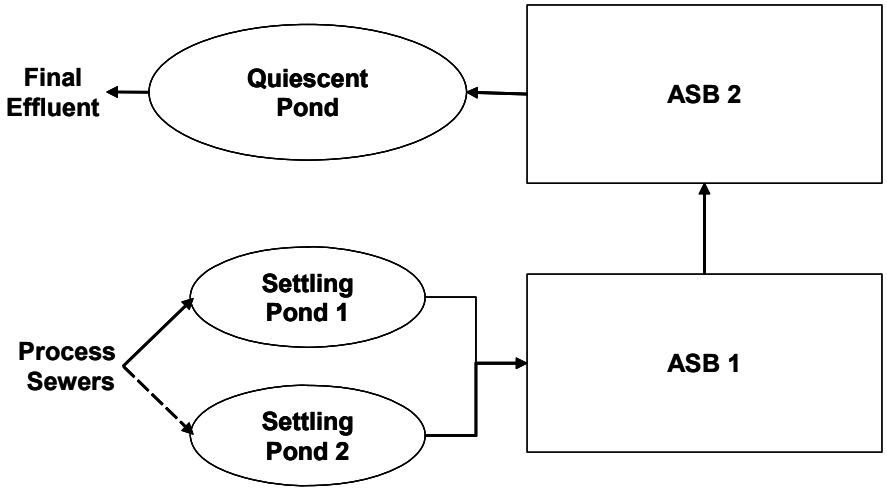

Figure B19. Mill U Wastewater Treatment Plant Schematic

Table B29. Mill U Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Settling Pond 2 Inlet	Settling Pond 2 Outlet	ASB 1 Inlet	ASB 1 Outlet	ASB 2 Inlet	ASB 2 Outlet	Quiescent Pond Outlet
Total sulfide	1690	4070	2580	2246	110	498	521
MeSH	59.4	120	49.1	30.2	ND	ND	ND
DMS	177	173	58.5	28.9	ND	ND	ND
DMDS	ND	ND	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL V

Mill V produces approximately 428,000 MTY of air dried kraft pulp, and 235,000 MTY of hardwood and softwood bleached kraft. The final product is 50% uncoated and 50% kraft board. A schematic of the WWTP is provided in Figure B20. Wastewater is treated using two 200 ft diameter (3.47 MG) and one 125 ft diameter (1.01 MG) primary clarifiers operating in parallel. Effluent from the primary clarifiers is injected with oxygen and nutrients prior to entering an aerobic digester. After digestion the wastewater is treated in three sequential aeration cells with 20 surface aerators. Water then flows into two 200 ft diameter (2.82 MG) and one 150 ft diameter (1.85 MG) clarifiers. Effluent from the secondary clarifiers passes through a reaeration cascade prior to final outfall. Samples were collected from the #3 primary clarifier inlet, three different zones across the clarifier, primary clarifier outlet, aerated digester, three zones of the aeration basin, and final effluent. Results are listed in Table B30.

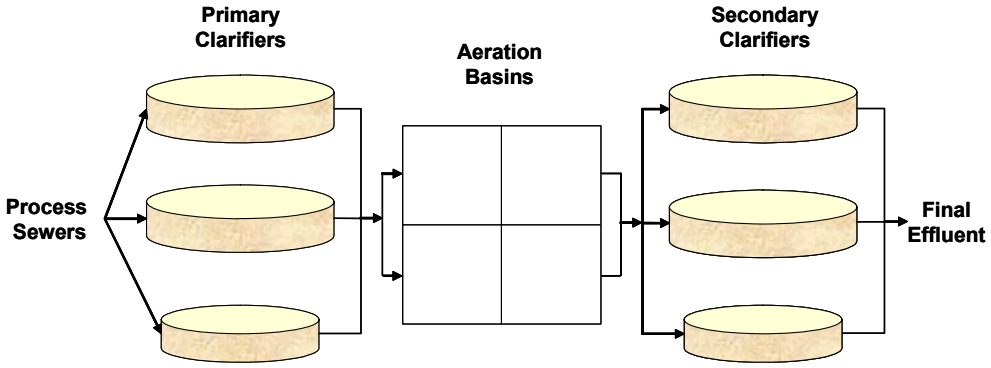

Figure B20. Mill V Wastewater Treatment Plant Schematic

Table B30. Mill V Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Primary Clarifier Inlet (n=4)	Primary Clarifier Middle (n=2)	Primary Clarifier Center (n=2)	Primary Clarifier Outlet (n=4)	AST Zone[a] (n=4)	Final Effluent
Mill V I						
Total sulfide	18100	10200	NA	8480	941	ND
MeSH	165	427	NA	168	ND	ND
DMS	404	497	NA	500	ND	ND
DMDS	159	ND	NA	49.0	ND	ND
DMTS	65	ND	NA	37.0	ND	ND
Mill V II						
Total sulfide	13300	7240	7116	19500	613	26.0
MeSH	500	381	309	700	30.7	ND
DMS	1021	486	480	1255	136	ND
DMDS	155	67.6	52.0	247	33.7	ND
DMTS	119	43.0	35.4	151	ND	ND

[a] average across all zones of the aeration basin

NA not analyzed during this sampling episode

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS